Elisabeth Schwarz, BSc

α,α’ – Phosphorus stabilised group 14 carbene analogues

MASTER'S THESIS

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Nicht weil es schwer ist, wagen wir es nicht, sondern weil wir es nicht wagen, ist es schwer.
Lucius Annaeus Seneca

AFFIDAVIT

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Kurzfassung

Tetrylene sind reaktive Moleküle, die ein Gruppe 14 Element (E = C, Si, Ge, Sn, Pb) in Oxidationsstufe +II enthalten. Elemente dieser Gruppe bevorzugen gewöhnlich die Oxidationsstufe +VI, was unter anderem die große Reaktivität dieser Verbindungsklasse erklärt. Tetrylene können sowohl als Lewis Basen als auch als Lewis Säuren reagieren, da sie gleichzeitig über ein einsames Elektronenpaar und über ein unbesetztes p-Orbital verfügen.

Zwecks Stabilisierung bedient man sich einerseits sperriger Substituenten, um die sterische Abschirmung des reaktiven Zentrums E zu erhöhen und andererseits kann die Reaktivität durch partielle Donierung von Elektronen in das leere Orbital an E durch benachbarte Atome wie z.B. Stickstoff (Arduengo Typ) oder ähnliches vermindert werden.

Während α, α'-N stabilisierte Tetrylene bereits gut untersucht sind, gibt es nur sehr wenige der Diphospha-analogen Verbindungen. Da die Größe der Atome, die geringere Elektronegativität und die stärkere Pyramidalisierung des Phosphor Atoms werden als Gründe dafür gesehen werden wurden in dieser Arbeit der Einfluss verschiedener sperriger und großer Substituenten auf DBP und dessen Derivativen untersucht. Mit DFT Berechnungen wurden Änderungen in der Planarität des Phosporatoms, Bindungslängen und der Winkel beobachtet. Um eine Einschätzung über die am besten für die Synthese geeingneten Substituenten zu erhalten, wurden Berechnungen für Silylene, Germylene und Stannylene mit unterschiedlichen Substituenten (^{i}Pr, ^{t}Bu, TMS, Ph, Hyp) durchgeführt. Durch die Rechnungen wurde bestätigt, dass sich vor allem sperrige Substituenten gut eignen und dass eine kleinere Pyramidalisierung des Phosphors eine stabilere Konfirmation zur Folge hat. Die Ergebnisse der Berechnungen geben Aufschluss auf die Farbe, die Bindungs- und Winkelverhältnisse in den zu synthetisierenden Verbindungen. Die Stabilität und Isolierbarkeit der unterschiedlichen Tetrylene wird mit einer Analyse der relativen Energien der verschiednen Konformere bestimmt.

*TMS = Trimethylsilan $SiMe_3$; Hyp = Tris(trimethylsilyl)silan $Si(SiMe_3)_3$

Abstract

Tetrylenes are reactive molecules which contain a group 14 element (E = C, Si, Ge, Sn, Pb) in oxidation state + II. Elements of this group commonly prefer the oxidation state + VI which, among other things, explains the high reactivity of this class of compounds. These compounds do not only have a lone pair, but also a unoccupied p-orbital and can, due to that, react as Lewis base and Lewis acid.

The stabilisation of these compounds can be increased by the use of bulky substituents, which makes it possible to increase the steric hindrance of the reactive center E. The other possibility of stabilisation is to reduce the reactivity by partial donation of electrons into the empty orbital of E by neighboring atoms such as nitrogen (Arduengo type).

While the α, α'-N-stabilized tetrylens are already well studied, there are very few oft he diphospha analogue compounds. The size of the atoms, the difference in electronegativities and the stronger pyramidalisation of the phosphorus might counteract effective orbital overlap, necessary for stabilisation. In the course of this thesis the influence of different substituents on 1,2-diphospinobenzene (DPB) are be investigated with calculations at the DFT level. DPB and its derivatives are suspected to be ideal candidates for the formation of P-stabilised cyclic tetrylenes. In order to get information about the best suitable substituent for the tetrylene synthesis, calculations of silylenes, germylenes and stannylenes were performed with various substitutes (^{i}Pr, ^{t}Bu, TMS, Ph, Hyp). The calculations led to the result, that bulkier substituents are more favourable not only because of the steric hindrance they also decrease the pyramidalisation of the P-atom and therefore increase the stability of the conformation. Their conformations and spectroscopic properties obtained by DFT calculations are analysed for future product identification.

*TMS = Trimethylsilane $SiMe_3$; Hyp = Tris(trimethylsilyl)silane $Si(SiMe_3)_3$

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Danke liebe Familie, dafür dass ihr immer für mich da seid! Muchas gracias, mi querida hermana ! Lieber Christoph:

Vielen Dank für die Blumen,
Vielen Dank, wie lieb von Dir,
Manchmal spielt das Leben mit Dir gern Katz und Maus,
Immer wird's das geben einer der trickst Dich aus,
Vielen Dank für die Blumen, vielen Dank, wie lieb von Dir. *Udo Jürgens*

Eli Schwarz
Graz, März 2015

Contents

Index of abbreviations

B	Beckes B88 functional
B3	Beckes 3-parameter hybrid functional
CGTO	contracted Gauss-type orbitals
DFT	desity functional theory
DZ	double zeta basis
ECP	effective core potential, Pseudopotential
ESDS	estimated standard deviations
eV	elektron-volt
GIAO	gauge invariant/independent atomic orbitals
GTF	Gauss-typ function
HF	Hartree-Fock
HOMO	highest occupied molecular orbital
Hyp	Tris(trimethylsilyl)silane
I	intensity
IR	infrared
iPr	isopropyl group
K	Kelvin
KS	Kohn-Sham
LCAO	linear combination of atomic orbitals
LUMO	lowest unoccupied molecular orbital
LYP	correlation functional von Lee, Yang, Paar
m-	meta
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
MO	molecular orbital
PHC	P-heterocyclic carbene

Ph	phenyl group
ppm	parts per million
SCF	self consistent field
STO	slater-type orbital
tBu	Tertbutyl group
TMS	Tetramethylsilan
TZ	triple zeta basis
UV	ultraviolet
VIS	visible
ZPE	zero point energy
$\boldsymbol{E}$	Energy
$\widehat{\boldsymbol{H}}$	Hamilton operator
$\boldsymbol{\phi}$	wave function of orbitals
$\boldsymbol{\Psi}$	total wave function of the system
$\boldsymbol{r}$	space coordinate
$\boldsymbol{\rho}$	electron density

Chapter 1

Introduction

1.1. State of the Art

In recent decades, it has generally been recognised that the role of carbenes has become increasingly important in modern chemistry.[1] As a result a noticeable number of stable carbenes have been isolated and investigated in detail. The chemistry of carbenes is now quite well-understood.[1]

Further attention has been paid to analogues of carbenes such as the N-heterocyclic (Arduengo) carbene, which was introduced in 1991.[2] These carbenes have become an important class of σ-donor ligands in coordination chemistry and catalysis.[3] With the synthesis of the first compound of this kind, a new way of catalysis and the possibility of the use as donor ligand opened up.
This milestone was followed by the important class of heavier silicon and germanium congeners. The first silicon example was reported by West[1] in 1994. Over the past 20 years, great effort has been put into the development, the adaptation and synthesis of higher carbene homologues. The chemistry of N-heterocyclic silylenes of type I,II and III has been well documented.[4] (Fig. 1.1)

The analogues (Si-Pb) with saturated backbones and a number of benzene-, pyridine-, naphthalene- and acenaphthene - annulated derivatives have all

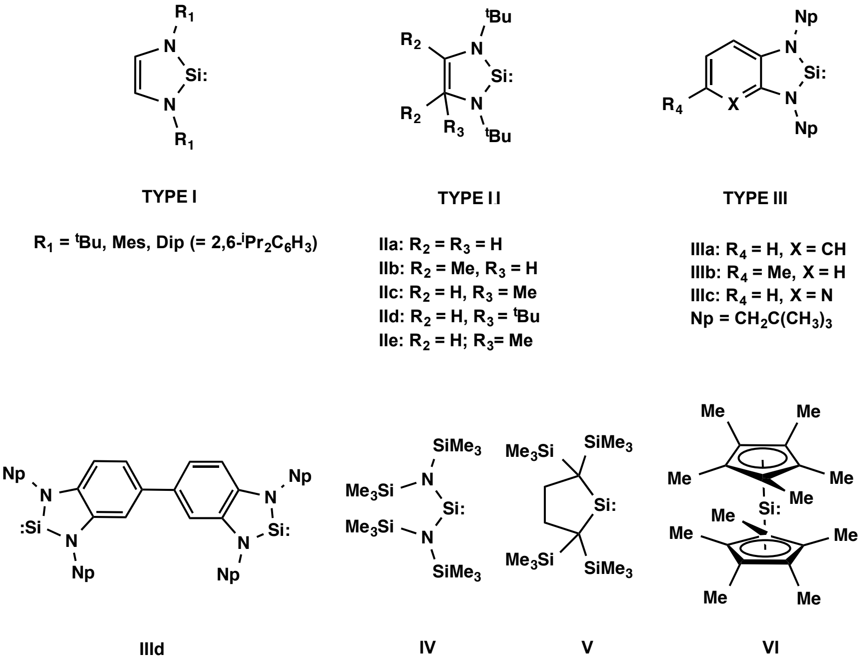


Figure 1.1.: Overview of N-heterocyclic silylenes[4]

been reported.[1] A good summary of all of these compounds can be found in *"Stable Heavier Carbene Analogues"*.[1]

Tetrylenes are uncharged compounds containing a group 14 element in the oxidation state of +II. These compounds occur in varying frequency from carbon to lead. There is an increasing energy difference of s- and p-orbitals of higher elements. This larger energy gap between the orbitals in the higher homologues can't be compensated by the hybridisation energy, as a result of which a twofold coordination and therefore oxidation state +II is preferred. Examples, such as $SnBr_2$ and $PbCl_2$ show that tin and lead prefer the oxidation state +II. Carbon and silicon tend to be stable in the state of +IV. Germanium is present in both, the +II and in the +IV state.
However, isolation in the +II state is only possible in coordination with a solvent or in a complex (e.g. $GeCl_2 \cdot$dioxane).
Carbenes, as well as other tetrylenes show sp^2 hybridisation, two orbitals are bonding to the substituents and in case of singlet tetrylenes, the third in plane sp^2 orbital is filled with an electron pair.

The main difference between the lightest tetrylenes, the carbenes, and their heavier congeners concerns the electronic ground state. The two free electrons of some carbenes avoid spin pairing and prefer a triplet ground state, while in the heavier tetrylenes these electrons are both found in the sp^2-orbital (lone pair character). The remaining p-orbital in upright direction is vacant. Via this empty p-orbital it is possible to accept electrons (Fig. 1.2).
In the singlet ground state tetrylens can react as electron donors and acceptors and are therefore Lewis-amphiphilic.

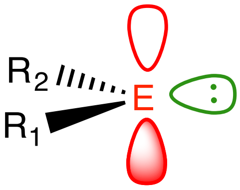


Figure 1.2.: Orbital scheme of tetrylenes

Tetrylenes feature a great reactivity, which makes it very difficult to isolate them under ambient conditions. The instability can be decreased by interaction with Lewis-basic substituents in α,α' - position. Thus the electrophilicity of the tetrylene can be lowered. With a cyclic backbone this effect can be increased, because the rotation of the substituents on the tetrylene is hindered. Another way to increase stability can be reached by the use of bulky substituents such as ^{t}Bu, ^{i}Pr, Ph, TMS and Hyp. This increases the steric shielding of the center E (= C, Si, Ge,Sn, Pb) and results in a kinetic stabilisation.

1.1.1. Diphosphatetrylenes

As noted above N-heterocyclic carbenes (NHCs) are common in chemistry, since they can be used in catalysis and as donor ligands. The Arduengo-type carbenes are stable at ambient conditions. The stability is enhanced by an electron rich backbone and bulky substituents on the nitrogens in α,α' position (σ - stabilisation). The lone pairs of the nitrogens can "push" electron density into the empty p-orbital, which causes an additional π - stabilisation. The rigidness and the positioning of the nitrogen lone pairs through the electron rich cyclic allyl backbone enhances the stabilisation.

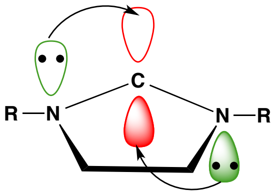


Figure 1.3.: Stabilisation of N-heterocyclic carbenes

A lot of work and research has been put into the development of this theme over the last two decades. Variations in the backbone and the sterically demanding groups located on the nitrogen atoms were investigated. It was noticed that the p-donor capabilities of the heavier group 15 elements (such as phosphorus) could be as large, or larger than those of their lighter counterparts (such as nitrogen).[5] Therefore, P-heterocyclic carbenes (PHCs) would be excellent candidates to complement NHCs.[5]
In contrast to the plethora of N-heterocyclic carbenes and their heavier group 14 analogues only one P-heterocyclic tetrylene is known in literature.[5] Apart from the difference in eletronegativities (Pauling: N = 3.04, P = 2.19) the stronger pyramidalisation of the phosphorus might counteract effective orbital overlap, necessary for stabilisation. These constraints explain the small number of diphosphatetrylenes compared to their nitrogen counterparts. Compared to the nitrogen counterparts even larger substituents are required for successful stabilisation. With the use of smaller and non-interacting substituents, dimeric structures are preferably formed. The tendency of dimerisation is the reason why most of the diphosphatetrylenes are dimers. Compounds were reported by du Mont (R = ^{t}Bu, ^{i}Pr E = Sn, 1977 and 1998[6]), Cowley (R = ^{t}Bu; E = Pb, 1988[7]) and Buhro (R = TMS, E= Sn/Pb[8]) (Fig. 1.4). The higher stabilisation is provided through head-to-tail cycloaddition. While NHCs are common, cyclic α,α'-P derivatives are scarce. To date there is only one cyclic diphosphatetrylene known in literature.[5]

In this compound the size of the supermesityl group (Mes*, (2,4,6-^{t}Bu)-Ph) was sufficient for stabilising. As mentioned before, the bulkiness and the sterical demand of the substituents have a big affect on the stability. There is the pos-

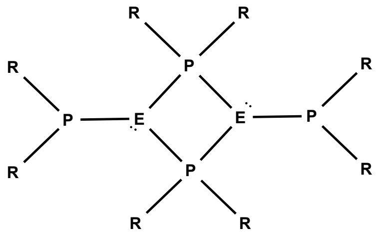


Figure 1.4.: Dimeric diphosphatetrylenes (R= ^{t}Bu, ^{i}Pr, TMS; E = Sn, Pb[6–8])

sibility of intramolecular interaction, like the head-to-tail cycloaddition in case of the dimers, which enhances the stability as well as using big and bulky substituents. Electron donors at the α, α' position or in side-groups of the substituents amplify this effect. The intermolecular stabilisation *via* electron donation through solvent molecules impacts the stabilisation positive.

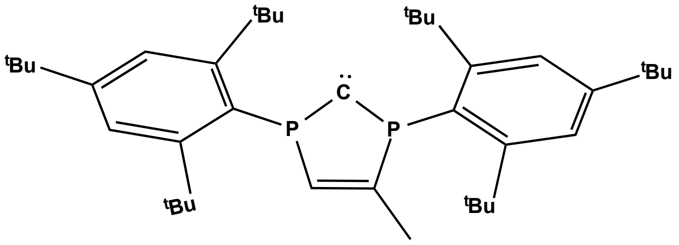


Figure 1.5.: P-heterocyclic carbene[5]

Therefore it is difficult to achieve the monomeric species. A monomeric diphosphatetrylene was synthesised by Driess in 2011.[9] (Fig. 1.6)

In this monomeric compound the substituents X (alkyl, aryl, OR, SR, and NR - groups) are particularly bulky and/or function as intramolecular donor centers.[9] Another group, which turned out to be suitable for the steric stabilisation of group 14 chemistry[10] is the TMS ($SiMe_3$) group. The cumbrous $Si(SiMe_3)_3$ group (hypersilyl) was also reported as a functional stabilising substituent.[11]

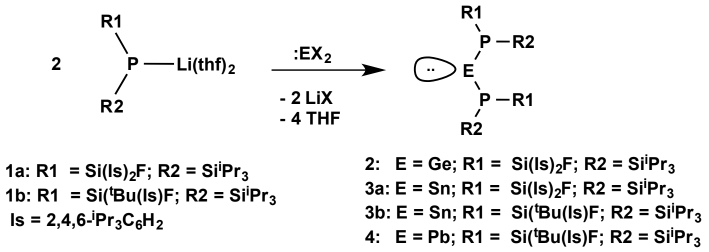


Figure 1.6.: Monomeric diphosphatetrylenes[9]

Through molecular modelling it is possible to estimate how various substituents influence the geometric structure and stabilisation of compounds. This makes it possible to estimate what compounds are suitable for synthesis.

1.2. Theoretical Section

This introduction is based on Peter W. Atkins' ”Physikalische Chemie”,[12] ”Essentials of Computational Chemistry-theories and models” by Christopher J. Cramer,[13] Neil S. Ostlund's ”Modern Quantum Chemistry”[14] and ”Quantum Chemistry” by Ira N. Levine.[15]

Density functional theory provides a powerful tool for computation of the quantum state of atoms, molecules and solids, and of ab-initio molecular dynamics. The foundation stone of todays DFT was the approximate version of Thomas and Fermi after the foundation of quantum mechanics in 1927. After that, Hohenberg, Kohn and Sham established the new DFT in the 1960s with their work ”Inhomogeneous Electron Gas”.[16] From that time on, density functional theory has grown vastly in popularity, and a flood of computational work in molecular and solid state physics has been the result.
The method has gained importance in recent years because it has some advantages, when compared with the Hartree-Fock-method, which are the following:
It is characterised by a lower computational complexity, shorter computation times and better matches with the experiments for the calculation of d-metals. Today, the DFT is the most commonly used method for the calculation of

molecular structures.[16]

The central parameter of the DFT is the electron density ρ instead of the wave function Ψ. The term "'functional"' in Density Functional Theory comes from the fact that the energy of the molecule is a function of the electron density $E_{[\rho]}$.[12] The electron density is a function of location, $\rho=\rho(r)$ and a function of a function is called functional. The energy of the ground state is described as follows.[12]

$$E_{[\rho]}=(E_{kin}+E_{p,EK}+E_{p,EE}+E_{p,Aus})[\rho] \tag{1.1}$$

E_{kin} is the kinetic energy of the electrons, $E_{p,EK}$ the potential energy of the electron-nuclear attraction, $E_{p,EE}$ the potential energy of the electron-electron repulsion and the exchange-correlation energy $E_{p,Aus}$, which takes all effects due to the spin in account.[12] The orbitals can be calculated from the Kohn-Sham equations. The electron density can be determined by applying equation (1.2).

To determine the electron density, the Kohn-Sham functions Ψ_i, which are *n* solutions of the Schrödinger-equation in an effective potential function v_{eff} were set off. The density is obtained from the sum of the electron densities of the Kohn-Sham equations:

$$\rho = \sum_{i=1}^{n} |\Psi_i(\vec{r})|^2 \tag{1.2}$$

The effective potential is dependent on the density:

$$v_{eff} = v(\vec{r}) + \int \frac{n(\vec{r})}{|\vec{r} - \vec{r}|} d^3r^{'} + v_{xc}(\vec{r}) \tag{1.3}$$

Here the first therm, $v(\vec{r})$, is the external potential which substantially describes the attraction of the electrons by the atomic nuclei, and the second term describes the electrostatic interaction of the electrons with each other (Hartree-term).

The solutions of the equations must be found iteratively, since the effective potential $v_{\text{eff}}(\vec{r})$ is dependent on the density $\rho(\vec{r})$ which itself is dependent on the solutions of these equations.[12] The third term $v_{\text{xc}}(\vec{r})$ is the so-called exchange correlation potential (”x”, ”exchange”, ”c” for ”correlation”) which ensures the correct treatment of multielectron systems.

A start-electron density is assumed, usually a simple superposition of the atomic electron densities. Then, the exchange-correlation potential is calculated. With this potential the Kohn-Sham equations can be solved to obtain a new potential. With this information it is possible to obtain a better approximation for the electron density. This process is repeated until a stable (self-consistent) solution is found.

The Kohn-Sham functions are pure calculation values and have no physical meaning by itself. Strictly speaking $v_{\text{eff}}(\vec{r})$ is dependent on the electron density at all sites and not just at the point $\vec{r}$, and can be calculated accurately for very few trivial cases. However, in practice this approach can often be used as an approximation of actual electron states. With DFT calculations, it is possible to determine the total energy of the atomic configuration. This, for example, can be helpful to find the most energetically favourable of several possible arrangements of a compound.

1.2.1. Basis Sets

Orbitals are wave functions, one-electron functions, eigenfunctions of an eigenvalue problem, the Schrödinger-equation for example, that describes the behaviour of an electron in three-dimensional space. These orbitals have no physical meaning, can have positive and negative values in different spatial areas and can, in principle, also be complex.

By the linear combination of functions, which should represent the orbital as well as possible, orbitals in atoms and molecules can be described mathematically.

$$\Psi_{\text{i}} = \sum_{r} c_{\text{ir}} \phi_{\text{r}} \quad (LCAO - method) \tag{1.4}$$

Originally the molecular orbitals were, according to the LCAO-method (LCAO = Linear Combination of Atomic Orbitals), approached by an actual linear combination of atomic orbitals.
Although it is common to use linear combinations of primitive Gaussian functions today, it is still spoken of LCAO. The most frequently used basis sets are the minimal STO-NG basis sets. Each contracted Gaussian function is formed from *N* primitive Gaussian functions. STO stands for Slater Type Orbital. In the most widely used STO-3G the contracted Gaussian functions are generated by three primitive Gaussian functions. Minimum basis sets are fixed and are unable to adjust to different molecular environments.

It is common to represent valence orbitals by more than one basis function, where each of which can be composed of a fixed linear combination of primitive Gaussian functions. One way to increase the size of a basis set is to take more basis functions per atom. Split valence basis sets, such as 3-21G and 6-31G basis sets, have two (or more) sets of basis functions for each valence orbital.
Basis sets in which there are multiple basis functions corresponding to each valence atomic orbital are called valence double, triple, quadruple-zeta, and so on, basis sets. Since the different orbitals of the split have different spatial extents, the combination allows the electron density to adjust its spatial extent appropriate to the particular molecular environment.

For a description of weakly bound electrons, such as anions, diffuse basis functions are required. An example of a basis set with diffuse basis functions is the 6-31+G. Polarisation is a constant in reality occurring phenomenon that cannot be described by the above definition of the basis set (minimum basis sets). To include the spatial dependence of the charge distribution of a molecule (eg. strongly polar molecules) additional basis functions of secondary quantum numbers are added. The more basic functions the basis set includes, the better is the approximation to the exact energy is. To characterise them, a * or a *d* (d-type functions added to atoms; f-type functions added to transition metals) are attached to the name. However, very complex basis sets do need more computing power which is coupled with an increase in costs. 6-31G* is

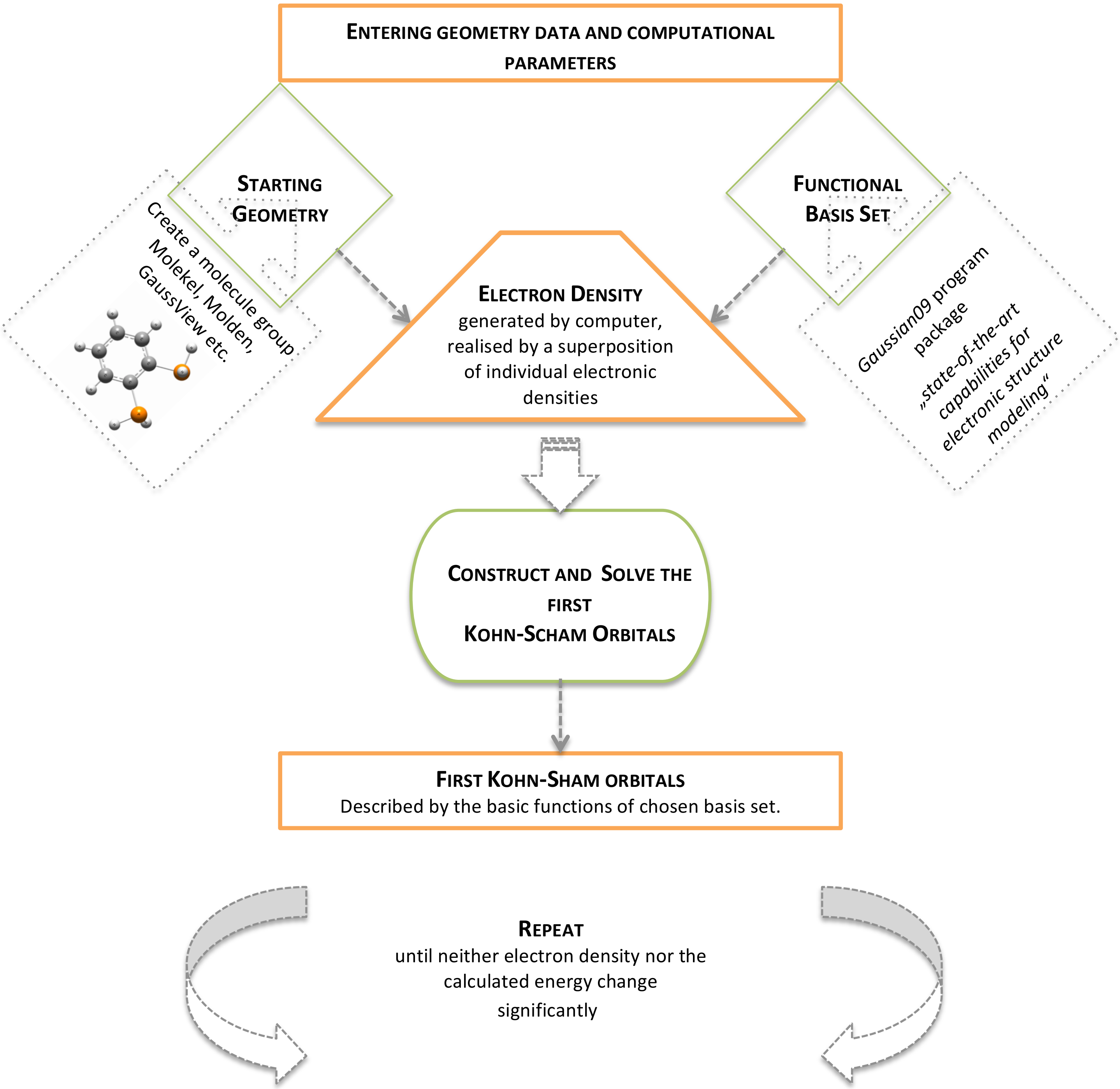
often considered the best compromise of speed and accuracy.
The notation of the previously mentioned basic sets, STO-NG, 6-31G, 6-31G*, 6-31+G*, is by J. Pople (Nobel Prize in Chemistry 1998).[17] In this work the 6-31+G* was used.

1.2.2. Functional

The choice of the right functional turns out to be complicated, because there is a multitude of different kinds of functionals with specific characteristics for each type of calculation. It has become evident, that for most calculations a hybrid functional, which includes a proportion of classical Hartree-Fock calculation, produces better results than those based only on the electron density.
Hybrid DFT is mixing various amounts of Hartree-Fock (HF) nonlocal exchange operator with DFT exchange correlation functionals.[18] In recent years, two methods have emerged as very promising the B3LYP and the mPW1PW91. With these methods it is possible to achieve accurate molecular structures, vibrational frequencies, and bond energies.
The fraction of HF exchange is set to 20% in B3LYP and 25% in mPW1PW91.[18] In this work the mPW1PW functional was used. This method is an modification of the functional proposed by Perdew and Wang and represents a very accurate gradient approximation.[19]

The results obtained from the mPW1PW91 model are close or even better than those obtained by the B3LYP method. Calculations, both for covalent and noncovalent interactions, are possible in a satisfactory theoretical framework encompassing the free electron gas limit and most of the known scaling conditions.[19]

General procedure of a DFT calculation



1.2.3. Optimisation

In order to determine a minimum, maximum or saddle point on the potential energy surface, it is necessary to build the first derivation. Critical or stationary points are defined as follows: the gradient decreases and converges to 0.

$$\partial E / \partial r_i = 0 \text{ for all } i \tag{1.5}$$

For determination of the local curvature of a function *f*, the Hessian matrix is used. This second derivation of the energy can be obtained, which makes it possible to determine the type of the critical point. If the Hessian is positive definite at r, then *f* attains a local minimum at r. If the Hessian is negative definite at r, then f attains a local maximum at r. If the Hessian has both positive and one negative eigenvalues then r is a saddle point for f (this is true even if r is degenerate).

The lowest energy structure obtained by the optimisation is used for the further operation. Also in this minimum there are oscillations which have influence on the total energy of the system. In order to obtain the correct energy in the ground state, the zero-point energy E_{ZPE}, the energy of these oscillations must be calculated.
Taking into account the 6 Degrees of Freedom (5 for linear molecules) and the fact that each of the *n* atoms vibrate in all directions, there are 3n-6 possible frequencies.
With these frequencies the energy of the vibrations E_{VIB} can be calculated.

Minima indicate a stable structure. A complete dissolution is too complex, it is therefore worked iteratively. The solution depends on the starting geometry.
With the minima a structure calculation, a calculation of reaction energies and a calculation of relative stability of isomers is possible. Saddle points are used for the calculation of transition structures of the reaction and the calculation of activation energy.

1.2.4. UV-Emission

With time-dependant DFT the singulet electron excitations can be obtained. This information makes it possible to interpret the colour of the calculated molecule.

The interpretation is an important point for the connection of synthesis and calculation of molecules. To know the colour of the desired product can be a big advantage in the synthesis.

1.2.5. Nuclear Magnetic Resonance (NMR)

The information obtained by an NMR calculation is the magnetic shielding of the nuclei. To compare the calculated shifts with the measured NMR data, one must calculate the magnetic shielding of the reference molecule (TMS for ^{1}H, ^{13}C, and ^{29}Si and PH_3 for ^{31}P).

This magnetic shielding is mathematically proportional to the second derivation of the energy change between the states with existing or absent external magnetic field. A magnetic field does influence the kinetic energy operator.

However, the grade of influence depends on the coordinates, so it is necessary to determine the origin of the coordinate system somewhere in the molecules. A magnetic field that acts from outside during an NMR experiment on a molecule is in this respect location-independent.

The dependence of the calculated shifts of location brings, except under very special conditions, incorrect results. These conditions include either the calculation of the exact wave function or the use of an infinitely large basis set, which is not possible in practical computational chemistry.

It is common to use the GIAO (”gauge invariant / independent atomic orbitals”)[20] approach. It is based on compensating the spatial dependence of the kinetic energy with the basic functions, which makes every calculated core to an origin and therefore location-independent. This approach is generally used and was also resorted to in this work it.

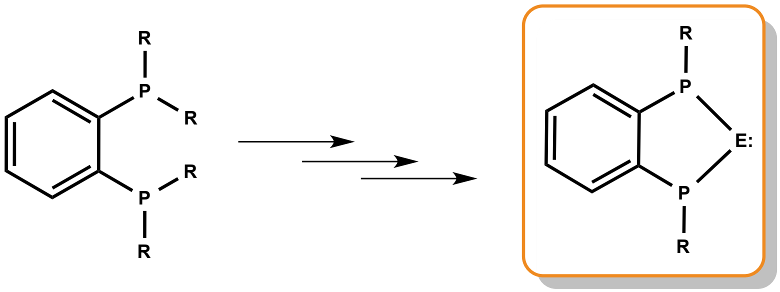
The computational details are found in the ”Results and Discussion” section.

1.2.6. Scope of work

As already mentioned, there are very few P-heterocyclic tetrylenes compared to N-heterocyclic carbenes. Diphosphines, sometimes called bisphosphanes, are organophosphorus compounds used as ligands in inorganic and organometallic chemistry. Due to their high reactivity phosphines are applied in many fields, such as catalysis.

The 1,2-diphosphinobenzene, abbreviated from now on as DPB, is a versatile building block and bifunctional primary aromatic phosphine which delivered several new organophosphorus compounds.[21,22] For the synthesis of 2-Organoelement-1,3-benzodiphospholenes DPB was used and might therefore be suitable for the synthesis of stable α,α' - diphosphatetrylenes.

Using DPB[21] the influence of different substituents (R = H,^{i}Pr, ^{t}Bu, Ph, TMS, Hyp) on phosphorus will be investigated with calculations at the DFT level. The conformations and spectroscopic properties of P-stabilised cyclic tetrylenes are analysed and used for future product identification. In the experimental part of this work DPB will be derivatised with various substituents on the phosphorus atom. With selected DPB derivatives, the synthesis of tetrylenes will be attempted *via* lithiation and reaction with group 14 halogen compounds or amides (Fig.1.5.).



R = H, ^{i}Pr, ^{t}Bu, TMS, Hyp, Ph
E = Si, Ge, Sn

Figure 1.7.: General reaction scheme: DPB derivatives to tetrylenes

Chapter 2

Results and Discussion

2.1. DFT Study

The DFT calculations make it possible to assess what structures are energetically favourable. Therefore it is possible to estimate how well a synthesis can proceed and what side products are possible. Another advantage is the estimation of the most stable structures, so that the interpretation of other data (eg NMR) becomes easier.
With the calculation of electronic excitations energies, the colour of the compounds can be estimated, which is a great advantage in the synthesis of coloured compounds.
Consequently the data obtained from the DFT study allows a more accurate interpretation of the reactions.

The main topic is the investigation of the influence of various substituents on the 1,2-diphosphinobenzene (DPB) ligand. Within molecular modelling, the advantages and disadvantages of using different substituents could be explored. The influence of different substituents on the pyrimidalisation of the P-atom, the bond lengths and angles in the compounds will be detected. The stability and structural differences of conformers can be determined.

With the calculations it is also possible to obtain information about possible tetrylenes, which is important for further product isolation. With the interpretation of the data, a prediction of favourable structures (e.g. preference of one conformer) is possible. A calculation of the electronic excitations allows a prediction of the colour of the compounds and the calculation of the NMR shieldings enables a comparison with measured values and facilitates peak assignment.

2.1.0.1. Geometries and characteristics of DPB derivatives

The influence of different substituents (H, ^{i}Pr, ^{t}Bu, Ph, TMS) on the phosphorus were investigated with calculations at the MPW1PW91/6-31+G* level. As mentioned before, DPB and its derivatives might be ideal candidates for the P-stabilised cyclic tetrylenes. Their geometric and spectroscopic properties obtained can be used for future product identification.

If we look at the reactants 1,2-bis(dimethoxyphosphoryl)benzene (compound ***1***) and DPB (compound ***2***) the calculated P-H, P-C, P-O, P=O, P-Si bond lengths [Å] are in an expected range (1.44 P-C, 1.84 P-C, 1.63 P-O, 1.50 P=O and 2.22 for Si-P[23]) (Fig. 2.2 and 2.1).

The DFT study predicts that the synthesis of compound ***1***, 1,2-bis(dimethoxyphosphoryl)benzene, should lead to a colourless product. The analysis of the electronic excitations gives a value of 240.95 nm, for the HOMO$\rightarrow$LUMO transition, which is not in the visible area (400 - 800 nm). The reaction solution was slightly yellow, the powder which was obtained from this solution by adding acetone and separation by centrifugation is colourless, which means that the calculation and the synthesis are in agreement.

The bond lengths between the C-atoms in the aromatic backbone do not differ with various substituents. A variation in the P-R lengths can be determined with various substituents, bigger substituents lead to shorter bond lenghts (Ph$<^{i}Pr)<^{t}Bu$. The planarity of the phosphorus atom changes with various substituents. In comparison with DPB, the pyrimidalisation of the phosphorus is smaller with substitution of the H atoms with bulkier substituents such as TMS and ^{t}Bu (Σ α(P) = 313.1° and 317.3°). Interestingly the sterically demanding phenyl group does not decrease the pyramidalisation (Σ α(P) = 306.2°). The smaller alkyl group (^{i}Pr Σ α(P) = 308.5°) is also less suitable, as summarised in Fig.2.2. This effect is important for a successful stabilisation of tetrylenes, because the stronger pyramidalisation of the phosphorus might counteract effective orbital overlap. Therefore a more planar character of the phosphorus atom would be favourable.

For referencing and comparison with the calculated data, a NMR measurement of the product purchased by Sigma Aldrich was performed.The measured NMR data of compounds ***1*** and ***2*** fits to the reported data in literature. The calculated results for all phosphorus shifts do differ from the measured ones by 16.5±4.63. The measured ^{1}H and ^{13}C also fit to the calculated data (Fig.2.1).

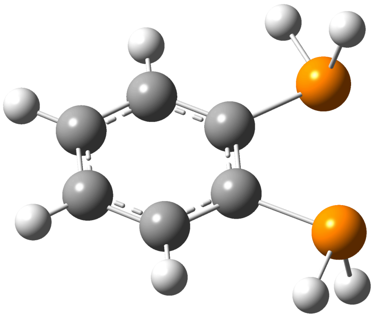
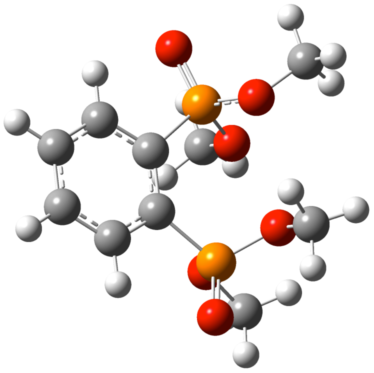
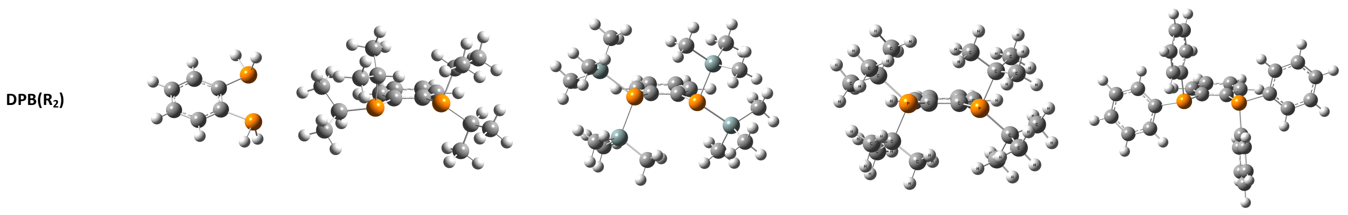
				
Compound	*1,2-Bis(phospino)benzene* ***2***		*1,2-bis(dimethoxyphosphoryl)benzene* ***1***	
Characterization				
UV	353.78 nm		240.95 nm	
Bond lenghts [Å]	P-H: 1.42 P-C1/C2: 1.86		P=O: 1.48 P – Ome: 1.60 P-C1/C2: 1.82	
NMR shifts [ppm]	*Calculation*	*Synthesis*	*Calculation*	*Synthesis*
^{13}C Ring	δ 134.99 δ 133.60 δ 126.15	δ 129.11 δ 127.01	δ 134.50 δ 128.17 δ 126.56	δ 130.48 δ 128.55
^{31}P	δ -107.16	δ -126.11	δ 23.26	δ 54.07
^{1}H				
C-**H**	δ 7.84 δ 8.09	δ 7.11		
P-H	δ 4.85 δ 5.57	δ 5.50		

Figure 2.1.: Comparison of calculated and measured values of compound ***1*** & ***2***

Considering the dipole moments, the compounds with alkyl rests have smaller values than the ones with aryl substituents. The dipole moment provides infor-



R	H	^{i}Pr	TMS	^{t}Bu	Ph
Dipole [D]	1.389	1.0447	1.1763	1.1864	1.4635
P-C [Å]	1.86	1.86	1.86	1.86	1.85
P-R [Å]	1.42	1.89	2.27	1.92	1.84
Σ α(P) [°]	289.1	308.5	313.1	317.3	306.2

Figure 2.2.: Comparison of mPW1PW91/6-31+G* calculated values for different substituents on DPB

mation about the molecular structure and interactions in the molecule. The size of the dipole moment allows the estimation of the solubility in various solvents and is thus advantageous for the synthesis.

As the TMS group showed the most promising properties for a further synthesis, two TMS substituted DPB derivatives (compounds ***3*** and ***4***) were investigated in more detail. Compund ***3***, $C_6H_4(PHSiMe_3)_2$-1,2, turned out to be no satisfying candidate for the further tetrylene synthesis, since two stereoisomers (d,l or *"trans"* and meso or *"cis"*) are formed (Fig.2.3). The *trans* conformer is more stable (E_{rel} = 16.01 kJ/mol), due to the hydrogen bond between a P lone pair and the hydrogen of the second phosphine group, resulting in a higher stability.

In the *cis* conformer the lone pairs face each other which destabilises the compound. For the metallisation via ^{n}BuLi the *cis* conformer would be favoured. The hydrogen bonding in the *trans* conformer decreases the possibility of a successful metallation and a further reaction to tetrylenes.

Therefore a compound where both H-atoms are substituted with bulkier moieties might be a better starting point for the tetrylene synthesis.

Compound ***4*** $C_6H_4(P(SiMe_3)_2)_2$-1,2 is a quite important molecule for the subsequent synthesis of the tetrylenes. The effects of the TMS group were compared to the results for other substituents (^{i}Pr; ^{t}Bu; Ph) on the P-atom (Fig.2.2). The TMS and the ^{t}Bu substituted DPB derivatives have a positive influence on the stability of the compound, which would make them a good candidates for the synthesis of tetrylenes.

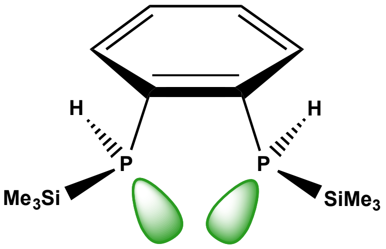
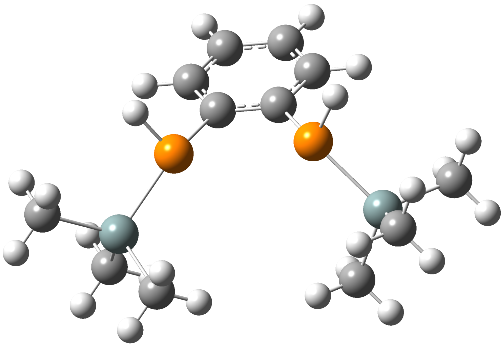
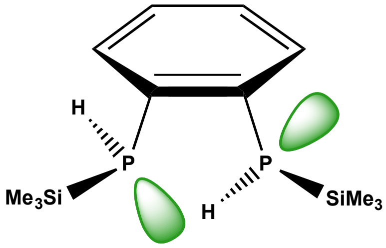
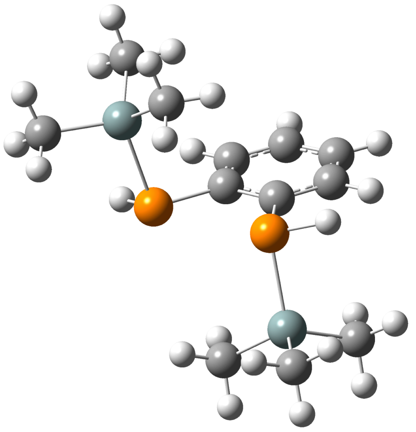
DPB(RR')$_2$		
R **R'**	**TMS** **H**	
E_{rel} [kJ/mol]	***cis* 16.01**	***trans* 0.0**
	 	 
P-C [Å] **P-Si (R) [Å]**	1.85 2.29	1.85 2.29
Si-P-C [°] **Σ α(P) [°]**	102.241 291.2	101.9 292.5

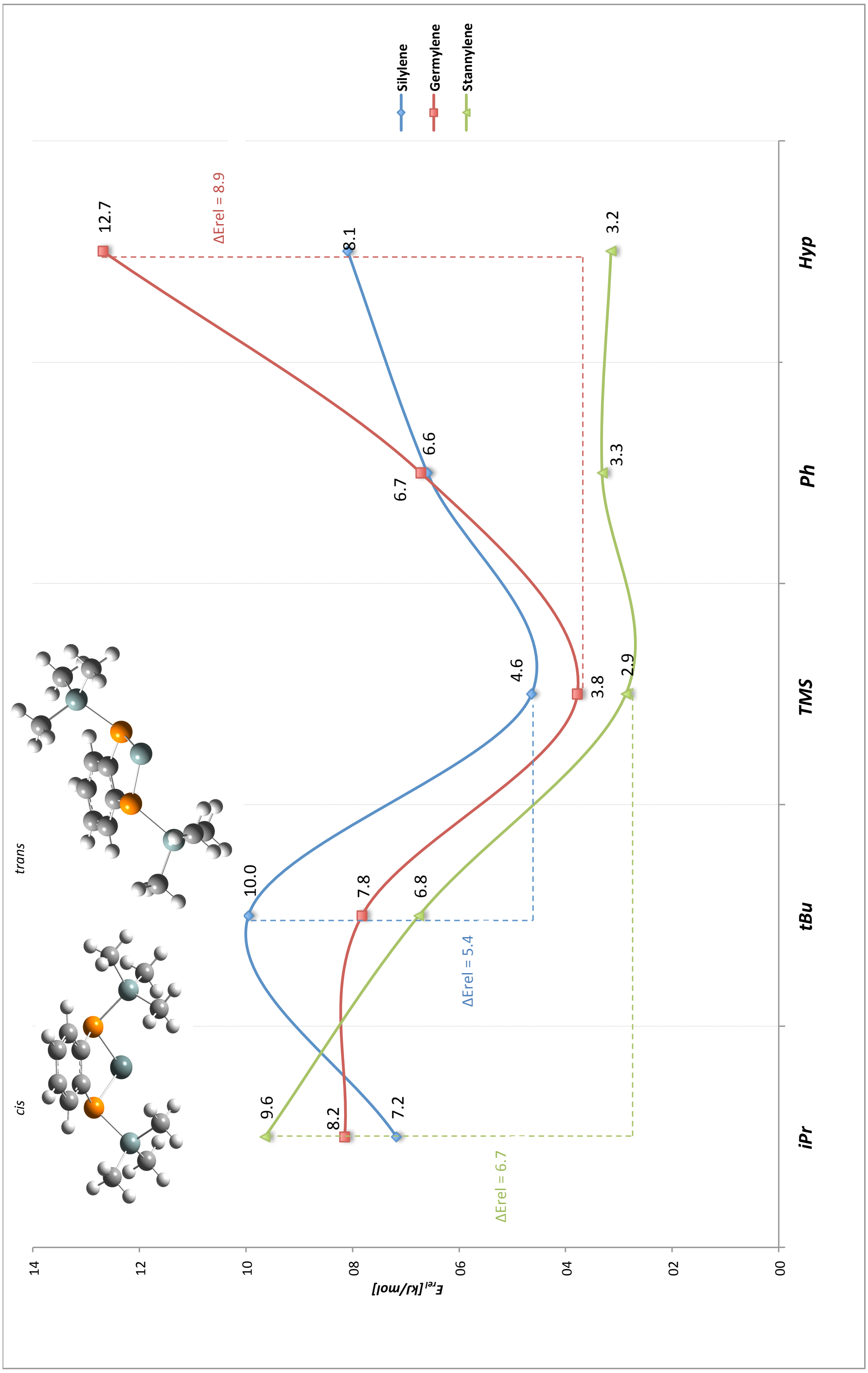
Figure 2.3.: Comparison: Isomers of compound ***3***

2.1.0.2. Tetrylenes

In the following tables the results of the DFT analysis for tetrylenes are summarised. As mentioned in the introduction, the phosphorus has a stronger pyramidalisation and a lower electronegativity than nitrogen, which is supposed to be the reason why P-heterocyclic compounds are rare. The DFT study is now extended on the stability and characteristics of the P-heterocyclic tetrylenes (E = Si, Ge, Sn). The influences of various substituents (^{i}Pr, ^{t}Bu, TMS, Ph, Hyp) on the planarity of the phosphorus were explored. Two conformers can be observed a d,l (*"trans"*) and a meso (*"cis"*) form. Due to steric reasons the formation of the *trans* conformer is energetically favoured (Fig.2.4). The *cis* form is sterically disadvantageous, because the bulky moieties do not have enough space. An analysis of the relative energies shows that the difference between the *cis* and *trans* conformer in the investigated homologues is very small. This indicates a mixture of both isomers should be expected in the synthesis.
All TMS substituted homologes have a very low energy barrier between the two conformers (silylene E_{rel} = 4.6 kJ/mol, germylene E_{rel} = 3.8 kJ/mol, stannylene E_{rel} = 2.9 kJ/mol,). The hypersilyl group on the other hand shows a bigger gap (silylene E_{rel} = 8.1 kJ/mol, germylene E_{rel} = 12.7 kJ/mol, stannylene E_{rel} = 3.2 kJ/mol). Therefore the isolation possibilities of tetrylenes (except stannylenes) could be improved with increasing the steric demand by using Hyp instead of the TMS.

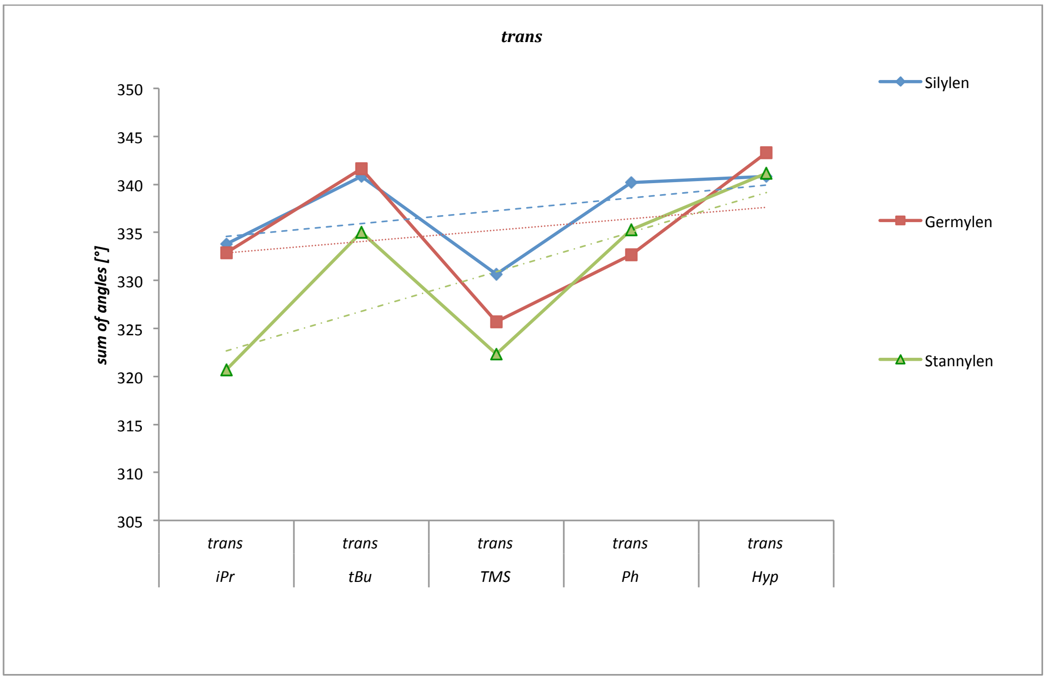
As shown in Fig.2.5 the planarity of the P-atom increases within the group. The pyramidalisation of the P-atom is smaller in the *trans* form. With all the substituents the *cis* form shows a higher pyramidalisation of the P-atom, which means that the orbital overlap could be hindered.

Less steric demanding alkyl groups are not profitable for decreasing the pyramidalisation of the P-atom. Also rigid aryl groups e.g. Ph do not effect the planarity of the P-atom in an extraordinary way. Although the Si-atom has a smaller electronegativity, the sterically demanding, bulky Hyp group does show the strongest influence of the pyramidalisation (Fig.2.5).



ΔE_{rel} = (highest – smallest E_{rel} value)

Figure 2.4.: Comparison of relative energies [kJ/mol] of tetrylenes with various substituents



Σ α(P) [°] *trans* conformation	Silylene	Germylene	Stannylene
^{i}Pr	333.8	332.9	320.7
^{t}Bu	340.8	341.6	335.0
TMS	330.7	328.7	322.3
Ph	340.2	332.9	335.3
Hyp	**340.8**	**343.3**	**341.2**

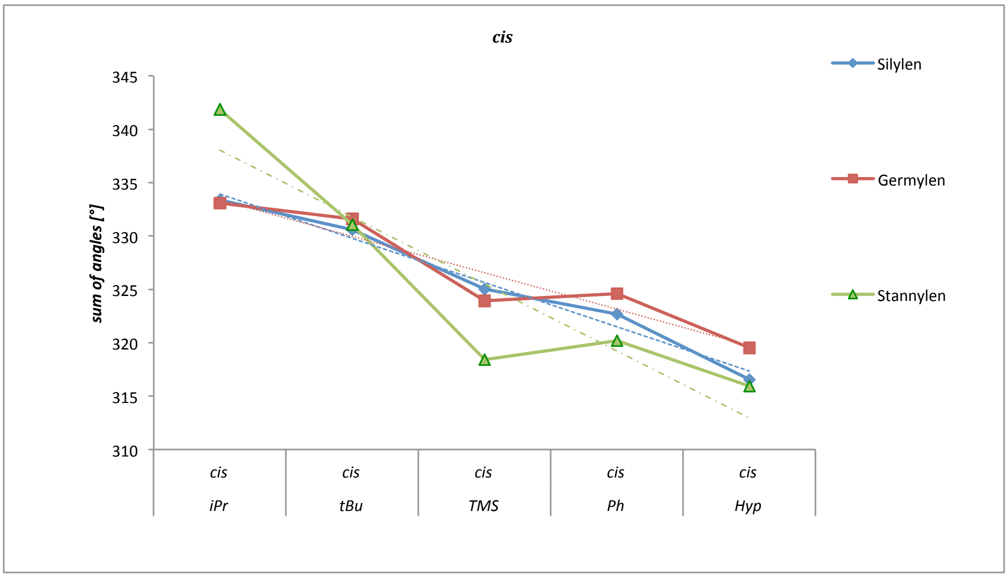


Figure 2.5.: Planarity of the P atom of tetrylenes in dependance of the substitution pattern

The geometric differences in the homologues with various substituents can be explored with the calculations. The E-P bond lengths increase within the higher homologues. The difference in the bond lengths is attributable to the atom sizes (Si<Ge<Sn) and the bulkiness of the substituents. The E-P bonds become longer with bigger, sterically demanding substituents (Fig.2.6). Interestingly the silicon containing substituents (TMS, Hyp) lead to shorter bonds, while the ^{t}Bu and the Ph group increase the bond lengths. Shorter bond lengths would be favourable for an effective orbital overlap.
The P-E-P angles are smaller in the higher homologues (2.7). The TMS and the Hyp substituents show an increasing angle compared to the alkyl and aryl groups. A smaller angle indicated a smaller pyramidalisation of the molecule, and therefor a higher stability. A general trend of increasing angles with bigger substituents can be seen. The smaller angles when moving down a group in the periodic table can be explained by the the expected decreasing hybridisations of the s an p orbitals for heavier main group elements.

With the calculation of the HOMO→LUMO values it is possible to obtain information about the colour of the products. As long as there is no interaction with solvent molecules, the calculation indicates colourless to yellow products for the silylenes, violet to green-blue products for the germylenes and red products for the stannylenes (Tab.2.1.). The analysis of the orbitals of $C_6H_4(P(SiMe_3)_2)_2Si$, $C_6H_4(P(SiMe_3)_2)_2Ge$ and $C_6H_4(P(SiMe_3)_2)_2Sn$ showed that the orbital overlap is more advantageous in the *trans* conformation. In the *cis* the LUMO and the HOMOs are as expected. The HOMO *trans* conformer splits in a HOMO-1 and a HOMO, in which an overlap of the lone pair of the P-atoms an the p-orbital of the tetrel atom can be seen (Fig.2.8). This increases the stability, which emphasises the assumption, that the *trans* conformation is more stable.

Table 2.1.: HOMO→LUMO excitation energies

Compound	**cis [nm]**	**trans [nm]**	**colour**
$C_6H_4(P(SiMe_3)_2)_2Si$	403.93	375.09	colourless - yellow
$C_6H_4(P(SiMe_3)_2)_2Ge$	574.20	638.12	violet - green-blue
$C_6H_4(P(SiMe_3)_2)_2Sn$	472.74	441.51	red

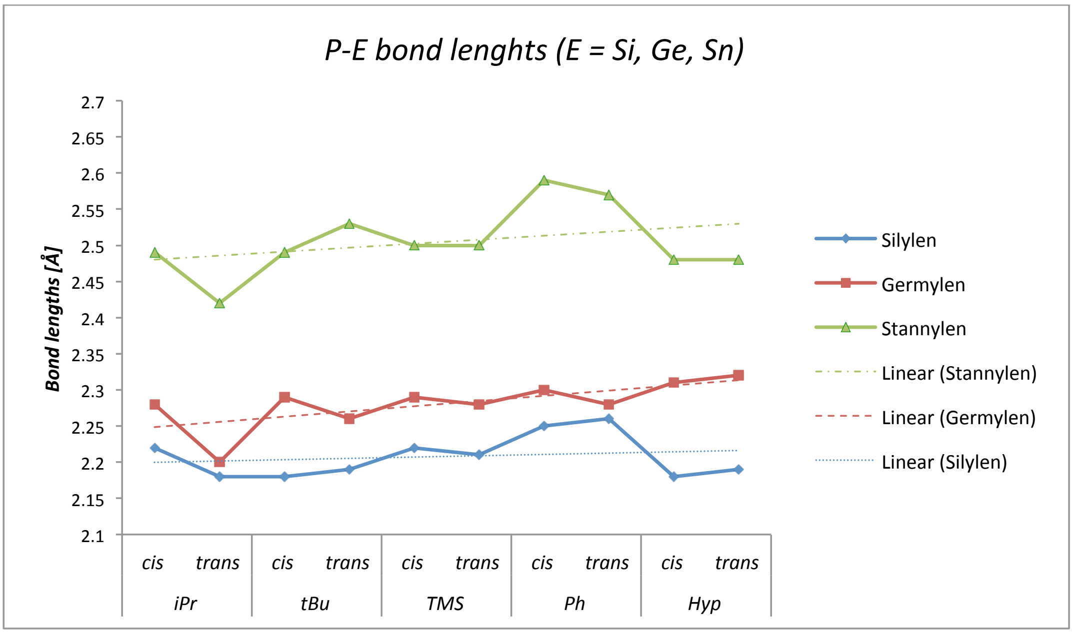


Figure 2.6.: Bond lengths of tetrylenes with various P-substituents

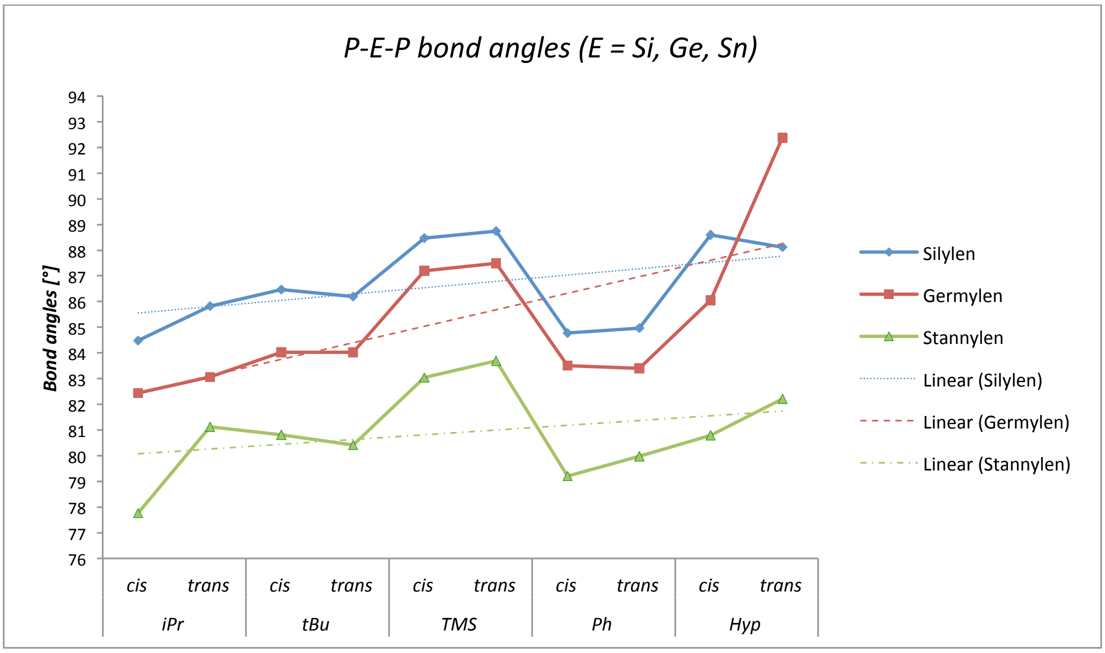


Figure 2.7.: Bond angles of tetrylenes with various P-substituents

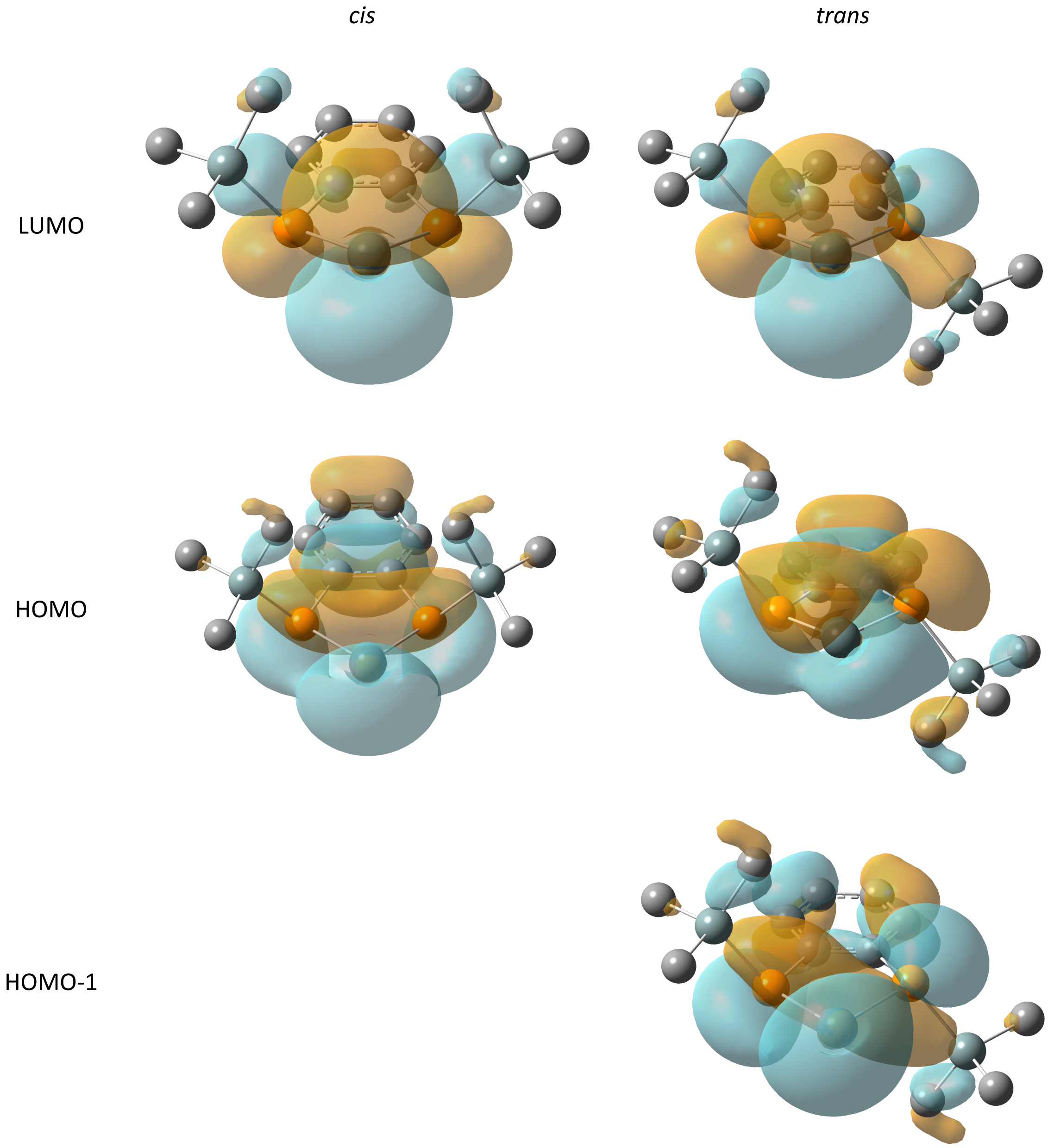


Figure 2.8.: Frontier orbitals of conformations of the investigated tetrylenes

2.2. Experimental Analysis and comparison with calculated data

2.2.1. DPB derivatives

As the DFT analysis showed DPB (1,2-diphospinobenzene) and its derivatives are ideal candidates for the formation of P-stabilised cyclic tetrylenes. Different reactions pathways are possible as starting point for the further reactions to tetrylenes (Fig.2.9). In order to increase the stability and protect the tetrel atom, the H-atom can be substituted with other groups (^{i}Pr, ^{t}Bu, Ph, TMS, Hyp). The one possibility is to replace only one hydrogen on each phosphorus atom with a different substituent, another option is to perform this step twice and thus replace all hydrogens with bulkier substituents. During this work, a substitution with TMS was examined, because this group showed promising properties for the synthesis and reaction mechanisms are known in literature.[24] The reaction pathways were investigated to determine which one is more advantageous for the subsequent reactions with group 14 halogen compounds (SiX_4, $GeCl_2$·dioxane, $SnBr_2$) or amides of the type ^{n}BuLi-E$(NMe_2)_n$ to form the desired tetrylenes.

The synthesis of compounds ***3*** and ***4*** (Fig.2.9) with the purchased DPB (*Sigma Aldrich*) were successful in good yields. The ^{29}Si of the reaction to compound ***3*** shows signals at 2.54 ppm (t), 4.10 ppm, and 4.42 ppm which can be compared to literature data (δ = 4.37 (t) and 4.65 (t) for $SiMe_3$[24]). The presence of more silicon shifts than expected, indicates a side product, or a not yet complete reaction. The spectra were taken during the reaction, to monitor the progress. For compound ***4*** a doubletic triplet at 2.59 ppm can be observed, which represents the two TMS groups on the phosphorus. The ^{31}P NMR patterns of both compounds are very characteristic (Fig.2.10 and Fig.2.11). A detailed investigation of these patterns by Hitchcock[24] showed the same results. The two main signals in the ^{31}P NMR spectra of compound ***3*** which are separated by a value of about 9.38 ppm might indicate the ratio of the *cis*/*trans* mixture. This was also discussed in literature.[24]

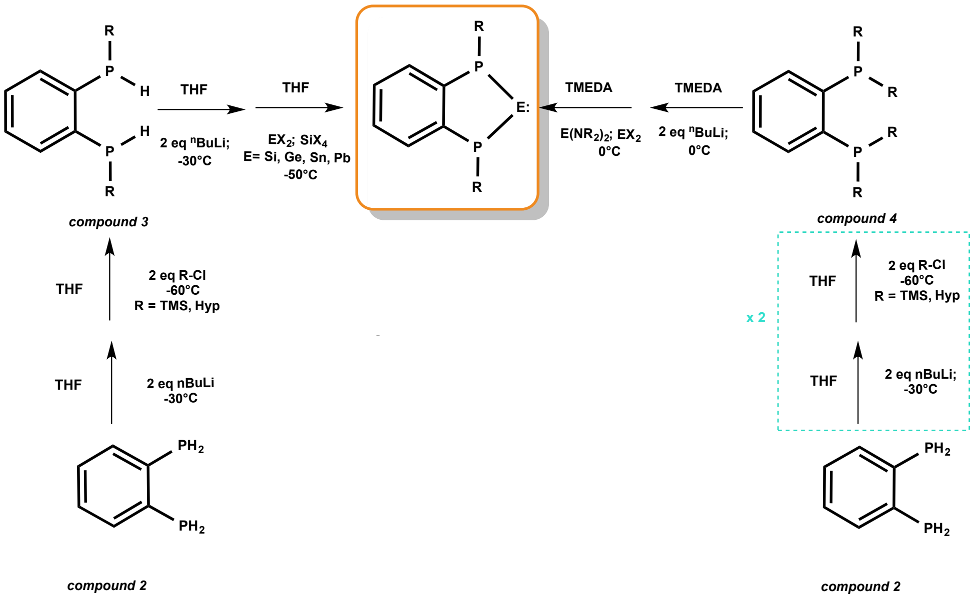


Figure 2.9.: General reaction scheme from 1,2-diphosphido-benzenes to tetrylenens

Table 2.2.: ^{31}P NMR data of compound ***3*** and ***4***

Compound	**Literature[24]**	**Meassurement**	**Calculation**
$C_6H_4(PHSiMe_3)_2$-1,2 *3*	-117,2	-115,1 (s/m)	-115,0
Synthesis of $C_6H_4[(P(SiMe_3)_2]$-1,2 *4*	-140,4	-138,7	-105,4

The synthesis of compound ***4*** is a sensible reaction. The reaction conditions have to be controlled very precisely. Even though it was mentioned in literature, that it is possible to perform the first and second step in one day,[24] this is just possible if the first step is completed. Therefore it is important to control all steps with a NMR measurement.

The purification achieved by filtration of each reaction step is important, because the side products (salts) cause problems in the crystallisation of the products.

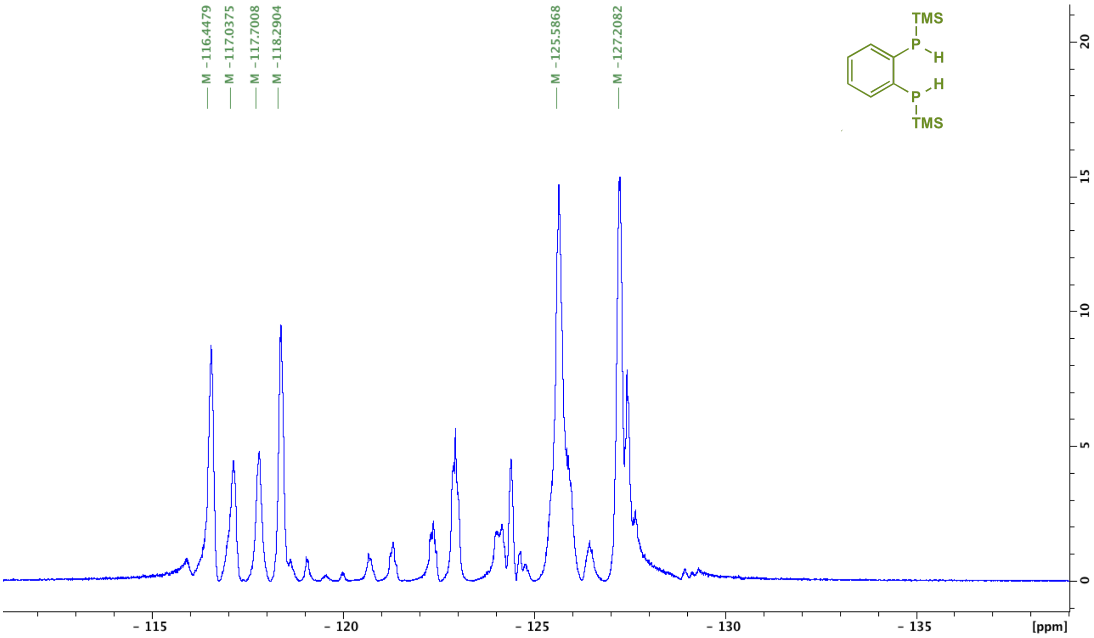


Figure 2.10.: ^{31}P NMR pattern of compound ***3*** (reaction solution)

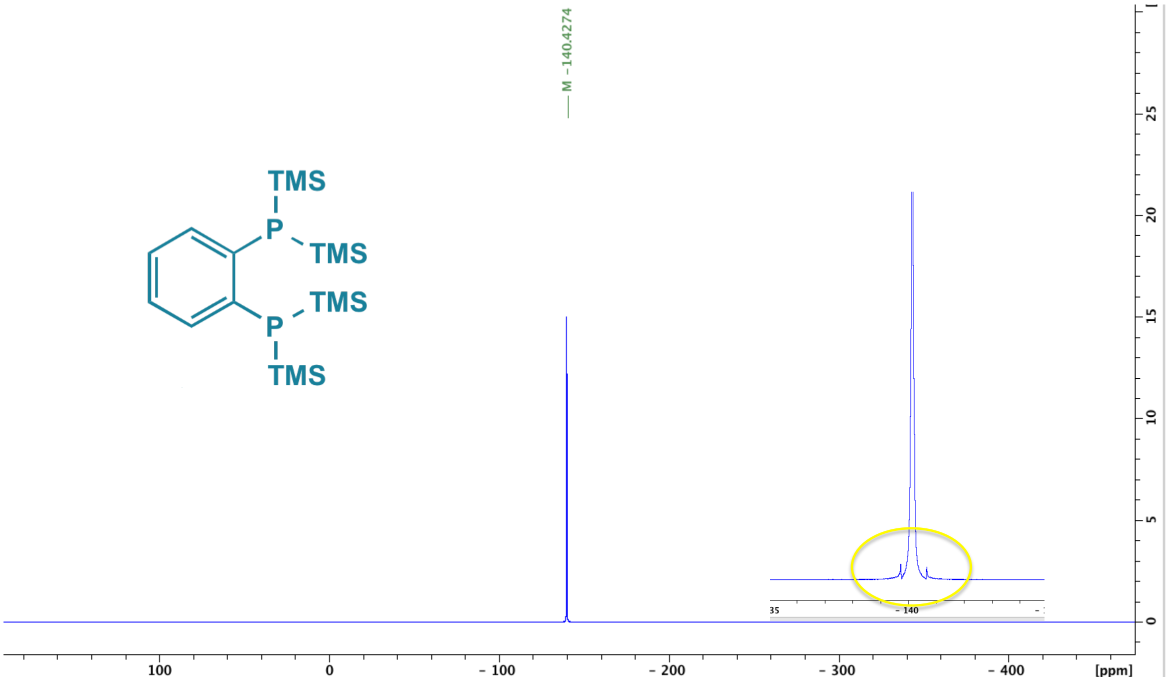


Figure 2.11.: ^{31}P NMR pattern compound ***4***

2.2.1.1. Synthesis of the reactand *DPB (1,2-Diphosphinobenzene) 2*

Because the reactions with the purchased DPB were successful, attempts for the synthesis of this starting material were made. Different types of lamps (Heraeus UV-RS 2, Aqua Cristal 5 W UV-C, HANAU 500 W medium pressure lamp) were used for the photolysis. So far the *Aqua Cristal 5 W UV-C* Lamp is the best choice for the experiment. The idea was, to perform the reaction with a low wattage lamp, which would be less expensive and could work without any additional cooling. This would make the reaction apparatus less complicated and would be convenient for long term irradiation.

Lamps with higher wattage (e.g. the Heraeus UV-RS 2) need an additional cooling system. The reaction itself needs to be heated up to 60℃. This temperature is essential. A reaction at room temperature did not show any results. A disadvantage of the low wattage is that the irradiation time increases. Nevertheless compound ***1*** (1,2- bis(dimethoxyphosphoryl)benzene) was obtained in small amounts, a further reaction to form DPB (compound ***3***) was not possible. The reaction was either carried out in hexane or without an additional solvent, which improved the reaction. To monitor the reaction progress of the photolysis, a NMR measurement was performed daily (Fig.2.12). The ^{31}P NMR data is compared to literature and calculated data in (Tab.2.3.). After 120 h an increase in product can be observed.

Table 2.3.: ^{31}P NMR data of compound ***1***

Compound	**Literature**[25]	**Meassurement**	**Calculation**
1,2-Bis(dimethoxyphosphoryl)benzene	$RPO(OR)_2$ 0–10 ppm $OP(OR)_3$ 0–2 ppm	2,70 ppm	23,3 ppm

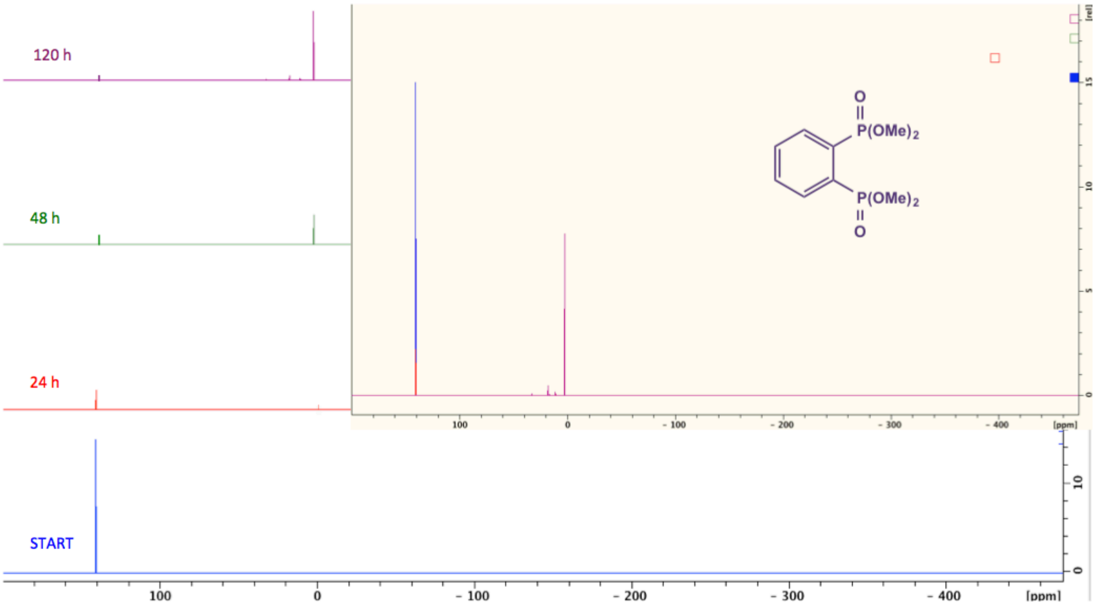


Figure 2.12.: Progress of photolysis reaction over time followed by ^{31}P NMR spectra

The obtained product is difficult to separate from the reaction solution, because it is a very fine white powder. It is not possible to filter it off, therefore the powder was centrifuged and the solvent was removed via syringe. The powder was dried by evaporating the solvent. A melting point *(mp ca.76 ° C)* could be measured and it fits to literature data.[26] The yield of the following reaction to produce DPB with a $Me_3SiCl/LiAlH_4$ mixture was very small, due to the small amount of compound ***1*** obtained in the first step. Enough compound could be isolated for a NMR measurement, which however did not show a clean product ***2***.

2.2.2. Tetrylenes

The tetrylene synthesis led to an considerable amount of information, which is very important and helpful for further investigation of these compounds. Different reaction pathways (Fig.2.13. A, B, C) for the generation of germylenes and stannylenes were investigated intensively.

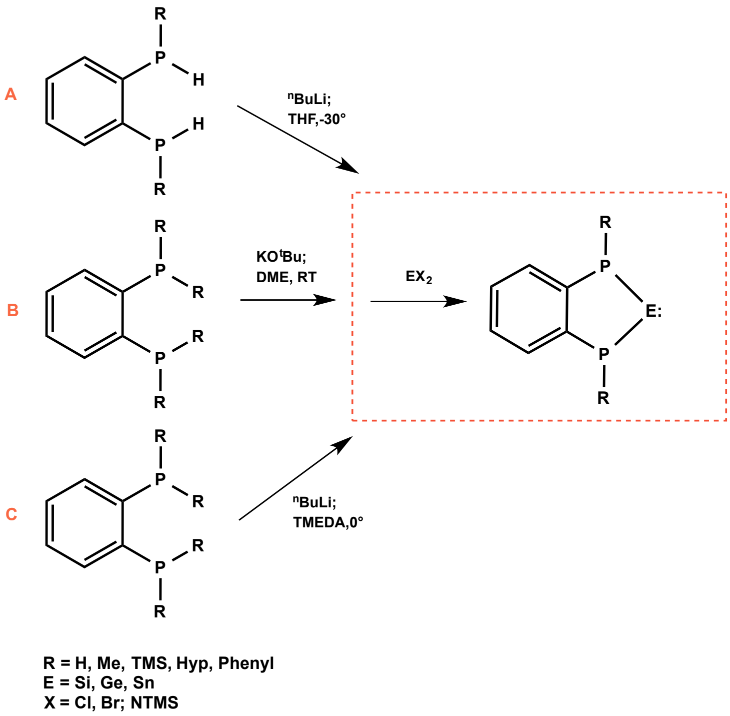


Figure 2.13.: Reaction pathways tetrylenes

2.2.2.1. Pathway A

Pathway A turned out to be unprofitable for the synthesis of both the germylenes and stannylenes. As mentioned before, there are two stereoisomers for compound ***3***[24](Fig.2.3), one stabilised by an intramolecular H-bond. Ultimately, it was not possible to obtain tetrylenes. Nevertheless, crystals which were obtained turned out to be an interesting germanium cluster. The crystal structure is discussed below.

In case of the stannylenes, the reaction always led to a dark-red solution, which turned brown with a brown, sparingly soluble precipitate. This process can be slowed down by storing the product in the cold (-80℃) and excluding light immediately after finishing the reaction. These tin compounds are very sensitive to air, temperature and light. Therefore and because of poor solubility, the brown precipitate could not be further analysed.

2.2.2.2. Results: Germanium complex compound ***5***

For solving the structure of the obtained crystals SHELXS97 (Sheldrick 2008) was used, to refine the structure SHELXL2014 (Sheldrick 2014) was used. All esds (estimated standard deviations), except the esd in the dihedral angle between two l.s. planes, are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

The germanium complex was obtained from the reaction of compound ***3*** with ^{n}BuLi and $GeCl_2$·dioxane in THF. The compound was filtered twice, because the salt was difficult to separate. After the second filtration in the dry box, a clean yellow solution could be obtained. The ^{31}P NMR data of the solution of this compound shows phosphorus shifts in a high range (127 ppm) which indicates a $P(OR)_3$ like side product. No silicon coupling to the TMS groups was detected. During purification the compound was exposed to oxygen, which reacted with the compound forming the interesting cage structure. The molecular structure of compound ***5*** with the atomic numbering scheme is shown in Fig.2.14, with pertinent bond lengths and angles given in Tab.2.4.. The crystallographic data is summarised in Tab.2.5.

The lithium is attached to the oxygen atom in a bridging coordination mode. The compound is a centrosymmetric dimer. This molecular species is structural similar to $[LiGe(OCH_2CH_2NMe_2)_3]_2$.[27] The common structural feature of the compounds found in literature[27,28] is a $E_2Li_2O_6$ cage, which is build of two $E_2Li_2O_3$ units, sharing a Li_2O_2 four-membered ring. This ring can also be found in the isolated germanium complex. However the complex does differ in the cage system, because there is an additional Li_2Cl_2 cage between the two $E_2Li_2O_3$ units. The structure of the Li_2Cl_2 cage has also been reported in literature,[29] but there is no equivalent known for a $E_2Li_2O_6Cl_2$ cage.

The ORTEP plot of compound ***5*** and a plot of a comparable structure are shown in Fig.2.15 and Fig.2.16. The obtained germanium complex is triclinic, which means a $\neq$ b $\neq$ c and $\alpha \neq \beta \neq \gamma \neq 90°$. The crystals were slightly yellow and block sized.

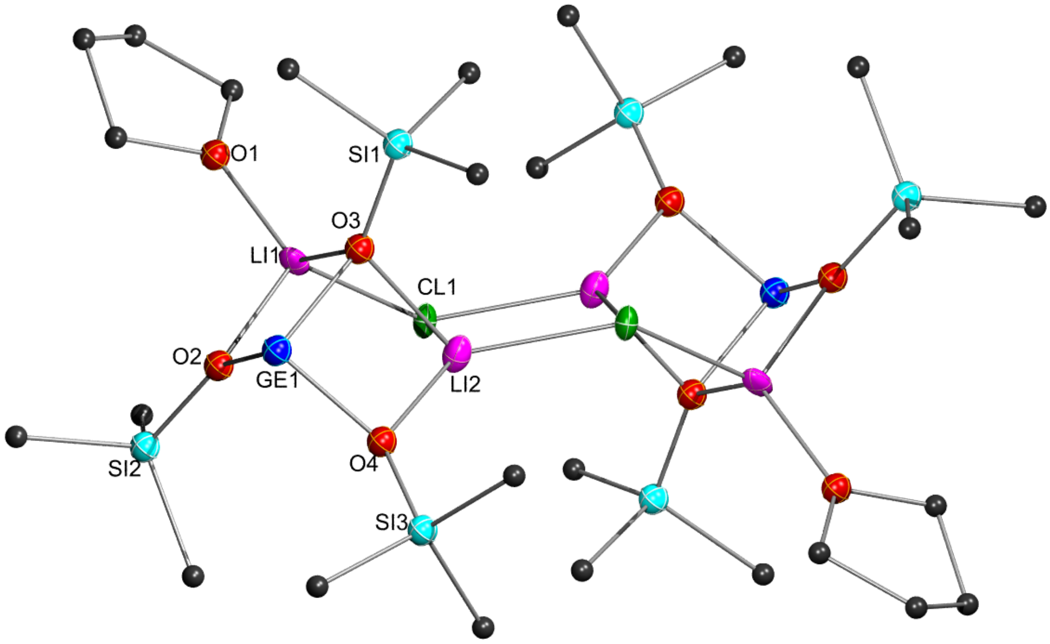


Figure 2.14.: Molecular structure of compound ***5***

bond lenghts [Å]	***5***	**Literature[27]**
Ge(1)-O(2)	1.876	1.876
Ge(1)-O(3)	1.933	1.954
Ge(1)-O(4)	1.887	1.888
O(2)-Li(1)	1.940	2.193
O(3)-Li(1)	1.989	2.019
O(3)-Li(2)	2.037	2.034
O(4)-Li(2)	1.949	-
O(2)-Si(2)	1.638	-
O(3)-Si(1)	1.647	-
O(4)-Si(3)	1.639	-
Li(1)-Cl(1)	2.312	-
Li(2)-Cl(1)	2.451	-
angles (°)		
O(1)-Ge(1)-O(3)	94.60	92.88
O(2)-Ge(1)-O(3)	87.29	88.09
Ge(1)-O(1)-Li(1)	97.42	100.7
Ge(1)-O(2)-Li(1)	93.98	98.10
Ge(1)-O(3)-Li(2)	91.64	94.80
Ge(1)-O(4)-Li(2)	95.87	98.50
O(1)-Li(1)-O(2)	82.65	78.6
O(3)-Li(2)-O(4)	82.80	100.0
Li(1)-O(3)-Li(2)	85.82	-
Li(1)-Cl(1)-Li(2)	69.75	-

Table 2.4.: Selected bond lengths (Å) and angles (°) compound ***5***

Compound	***5***
Empirical formula	$C_{26}H_{70}Cl_2Ge_2L_4O_8Si_6$
Formula weight (g/mol)	923.20
T(K)	100
n **Wavelength [Å]**	0.71073
Crystal System	Triclinic
Space group	$P^{-}1$
Unit cell dimensions	
a(Å)	10.932
b(Å)	11.136
c(Å)	12.772
a (°)	78.768
b (°)	65.768
c (°)	62.688
V (Å^3)	1259.7
Z	1
Density(calc.) (mg/$^{-3}$)	1.217
Absorption coefficient (mm^{-1})	1.48
F (000)	484
Crystal Size (mm)	0.20 x 0.18 x 0.13
Crystal habit	Block, yellow
2θ range (°)	2.3–27.3°
Index ranges	$-13 \leq h \leq 14$
	$-14 \leq k \leq 14$
	$-16 \leq l \leq 16$
Reflections collected	14344
Independent felections	5588
No. Of Parameters	226

Table 2.5.: Crystallographic data for compound ***5***

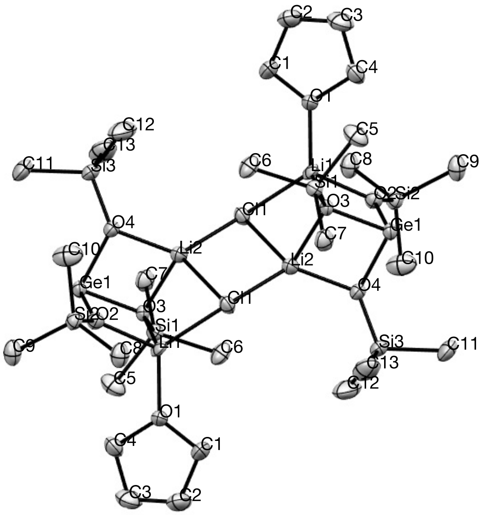


Figure 2.15.: ORTEP Plot: $Ge_2Li_2O_6Cl_2$ cage (compound ***5***)

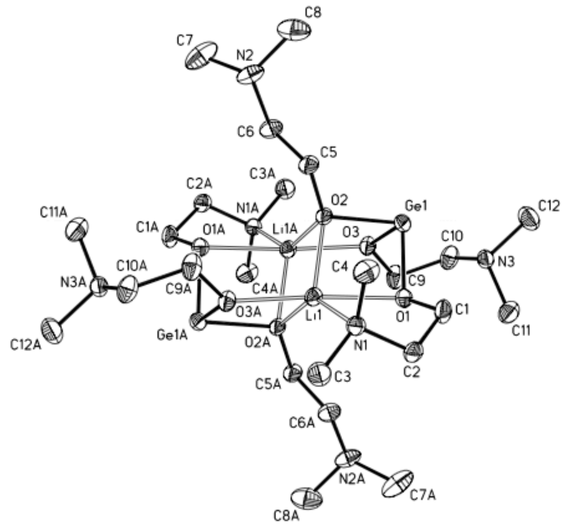


Figure 2.16.: ORTEP Plot: $Ge_2Li_2O_5$ cage[27]

2.2.2.3. Pathway B

Because of the problems caused by the stereoisomers, pathway B, with two bulky substituents on each P-Atom, opened up as alternative. The cleaving of two TMS groups with 2 equivalents KO^tBu in the first step o pathway B led to a bright red clear solution. KO^tBu is known to cleave P-Si bonds of $P(SiMe_3)$.[30] In this case a controlled reaction is quite difficult to achieve, a specific splitting of two TMS groups is challenging.

The ^{31}P NMR showed a broad signal (-96.76 to -100.68 ppm) in an expected ppm range for a P-K interaction (-99.6 ppm).[31] The ^{29}Si NMR spectra showed characteristic signals for ($^tBuOSiMe_3$), but no P-Si coupling. One part of the solution was kept for crystallisation and detailed analysis, but no clean product could be isolated. The other part was used for further reactions with $SnBr_2$, which led again to a red brown solution and a brown precipitate, which could not be further analysed.

2.2.2.4. Pathway C

Pathway C led to the most promising results. Mixed-base systems of the type $^nBuLi-E(NMe_2)$ are highly effective in the multiple deprotonation of simple organic molecules.[3]

The reaction with $^nBuLi-Sn(NTMS_2)$ led to a red solution. Red Crystals could be obtained which are very sensitive to light. When exposed to light for more than 10 minutes a colour change from red to light yellow and brown occurs. Therefore and because of the minor quality of the crystals no measurement was possible.

The results of this step are so promising because the red colour is, according to the calculations (see "DFT Study") an indication for the desired stannylene. Also the ^{119}Sn NMR shift is in an expected range (Tab.2.6.) according to the calculations.

After recrystallisation in toluene at -30° C, red to orange crystals, which are very sensitive to air, temperature and light could be obtained. The measurement was difficult, because the crystals can't be exposed to light for more than 7 - 10 minutes. The crystals should be stored at reduced temperature $\leq$-30°.

The recrystallised crystals led to an interesting crystal structure wich is discussed below, which does not correspond to the desired product. The obtained structure does not include phosphorus. The measured ^{31}P shifts of the solution differ from the DPB reactant. However the shifts do not fit the calculated data or comparable data in literature. The existing stannylene dianion $[C_6H_4P_2Sn]^{2-}$ shows a singlet δ = 238.0 ppm in the ^{31}P spectra[3] and a triplet δ = 1340.3 ppm in the ^{119}Sn spectra.[3] The free diphosphatetrylene Sn(PHypTMS)$_2$, which was mentioned in a PhD Thesis of the University of Technology in 2015[32] shows a shift in the ^{119}Sn NMR of 1466.7 ppm. The value of the obtained structure is with 770.8 ppm very low and it indicates that is shouldn't be assigned to the diphosphatetrylene.

Table 2.6.: Calculated NMR data of stannylenes and measured values tin containing synthesised compounds

Stannylene	Calculation [ppm]	Measurement [ppm]
^{13}C		
cis	115.9; 127.5; 118.9 ring	116.7
	6.48; 6.77; 6.70 Si(CH$_3$)	5.41
trans	147.2; 127.9; 119.4 ring	116.7
	7.57; 5.68; 5.39 Si(CH$_3$)	5.41
^{29}Si		
cis	-4.95 Si(CH$_3$)	-1.74
trans	-3.94 Si(CH$_3$)	-1.74
^{31}P		
cis	88.8	- 36.80
trans	87.5	-36.80
^{119}Sn		
cis	1347.4	770.8; 376.6
trans	1628.5	770.8; 376.6

To sum up it can be said that the germylenes as well as the stannylenes are very sensitive to temperature and air. The tin compounds should be stored at least at -50°C and in absence of light.

2.2.2.5. Results: Tin compound *6* obtained by reaction pathway C

X-Ray investigation of the red-orange tin crystals has shown that pathway C led to an separated ion pair with an anionic tin compound, [Sn(NTMS$_2$)$_3$]$^-$, and the TMEDA coordinated Li cation bis(N,N,N',N'-tetramethylethylenediamine)lithium(1+) (Fig.2.17).

This is an very interesting compound which was not known yet. There are just few comparable compounds found in literature. There is one anionic [(Ph$_3$)Sn)$_3$Sn]$^-$ complex of ytterbium. The cation of this compound is a centrisymetrical dimer in which two Yb atoms are each bonded to three chelate DME molecules and related by two bridged chlorine atoms.[33] These crystals were yellow-brown and also unstable in air. There are also some tin(IV) bis(trimethylsilyl)amides in literature[34] which can be used for the comparison

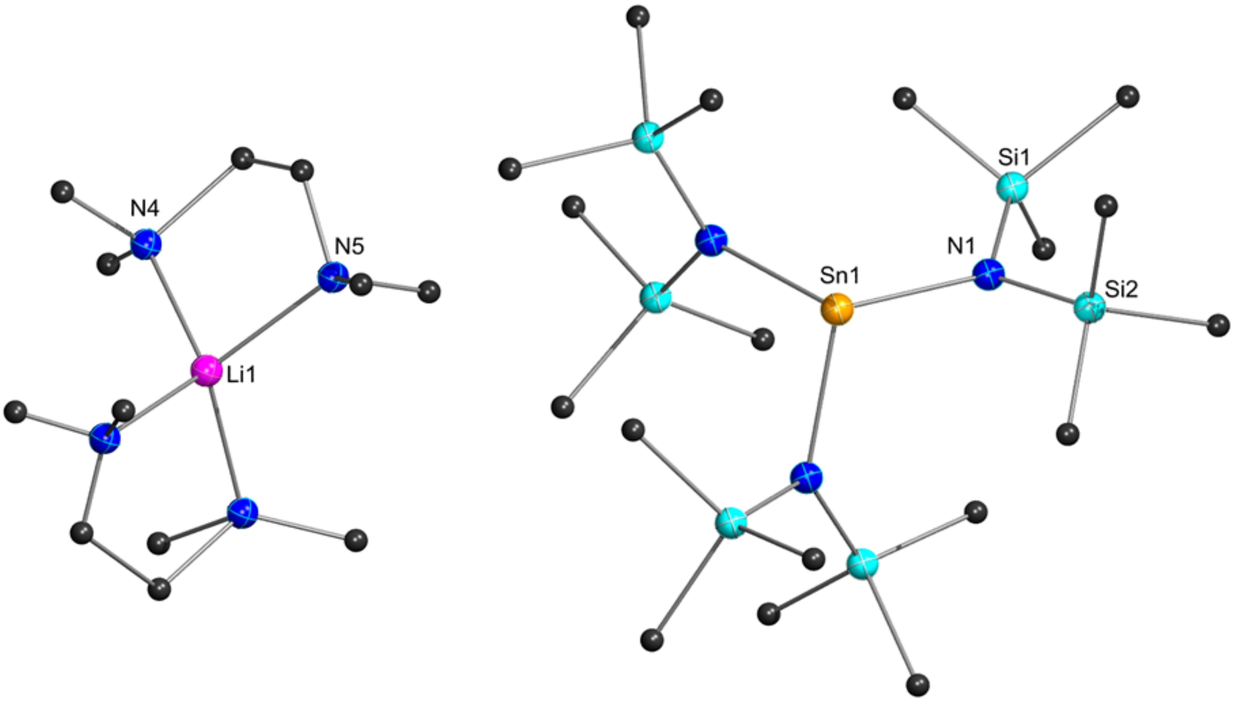


Figure 2.17.: Crystal structure of $[Sn(NTMS_2)_3]^-$ ***6***

of the Sn-N bond lengths and ^{119}Sn NMR shifts.

The unusual anion has a pyramidal structure (angle sum = 309.1 °), the central Sn atom is bonded to three $N(TMS)_2$ groups. The bond lengths and angles are summarised in Tab.2.7. and the crystallographic data is summarised in Tab.2.8.. The original pathway (C Fig.2.18) should lead to a stannylene. For the formation of the obtained anionic structure, several options exist. There is the possibility that in the formation of the starting materials a by-product, $LiN(TMS)_2$, was created, which led to the formation of the crystal structure. The ^{1}H (0.27 ppm), ^{13}C (6.39 ppm), ^{29}Si (-1.74 ppm) and ^{119}Sn (757.0 ppm) NMR shifts of $Sn(TMS_2)_2$ do fit to literature.[35] However due to the small amounts, this product was not distilled, which could be the reason for an unclean product and the unusual reaction products. The ^{31}P (-151.66) and the ^{29}Si (-5.36) shifts of $Li(tmeda)_2[(C_6H_4(P(SiMe_3)_2)\text{-}1,2]$ are also comparable to literature data.[24] The amounts of both compounds were small, a slight stoichiometric deviation could change the reaction pathway. It could also be possible that the desired product is still in solution, however there was no Sn-P coupling visible in the NMR spectra. The exact mechanism of this reaction is yet to be investigated.

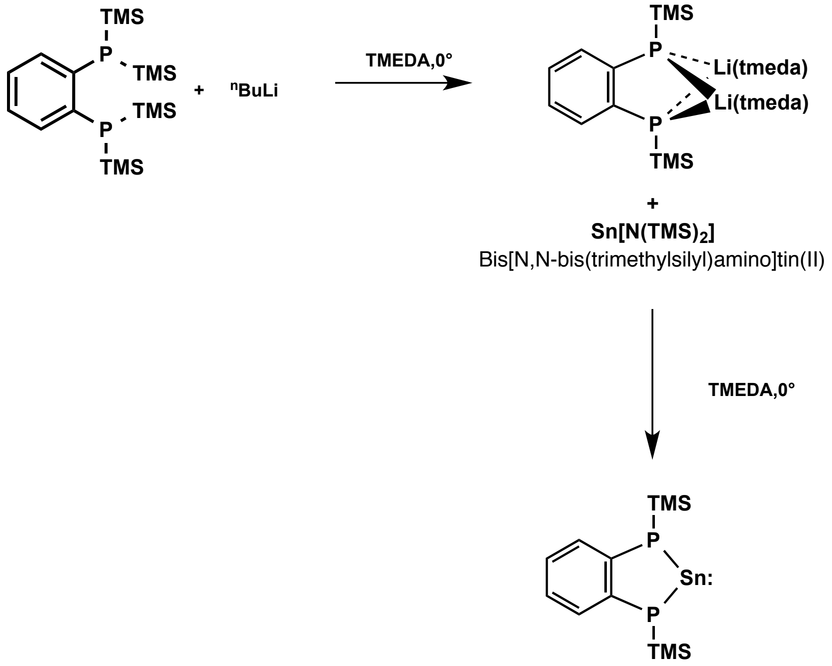


Figure 2.18.: Reaction pathway C for stannylenes

bond lenghts	**$Sn(NTMS_2)_3$ *6***	**Literature[34,36]**
Sn(1)-N(1)	2.25	2.05
Sn(1)-N(2)	2.22	2.05
Sn(1)-N(3)	2.24	2.05
N(1)-Si(1)	1.77	1.77
N(1)-Si(2)	1.75	1.77
Li(1)-N(4)	2.10	2.09
Li(1)-N(4)	2.10	2.09
angles		
N(1)-Sn(1)-N(2)	104.4	116.05
N(2)-Sn(1)-N(3)	106.1	-
N(3)-Sn(1)-N(1)	98.9	-

Table 2.7.: Selected bond lengths (Å) and angles (°) compound ***6***

Compound	**$Sn(NTMS_2)_3$ *6***
Empirical formula	$C_{18}H_{54}N_3Si_6Sn{\cdot}C_{12}H_{32}N_4Li$
Formula weight (g/mol)	839.23
T(K)	100
n **Wavelength [Å]**	0.71073
Crystal System	Monoclinic
Space group	$P2_{1/n}$
Unit cell dimensions	
a(Å)	16.7323 (8)
b(Å)	46.597 (2)
c(Å)	19.9225 (13)
a (°)	90
b (°)	107.7101 (15)
c (°)	90
V ($Å^3$)	14797.0 (14)
Z	24
Density(calc.) ($mg/^{-3}$)	1.536
Absorption coefficient (mm^{-1})	1.15
F (000)	6600
Crystal Size (mm)	0.09 x 0.04 x 0.01
Crystal habit	orange plate
2θ range (°)	0.9–23.4
Index ranges	$-13 \leq h \leq 14$
	$-14 \leq k \leq 14$
	$-16 \leq l \leq 16$
Reflections collected	14344
Independent felections	21476
No. Of Parameters	525

Table 2.8.: Crystallographic data for compound $Sn(NTMS_2)_3$ ***6***

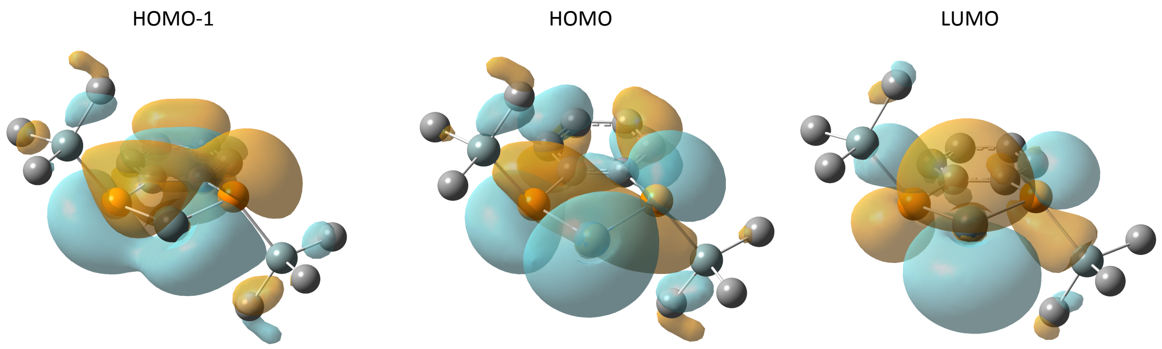
Chapter 3

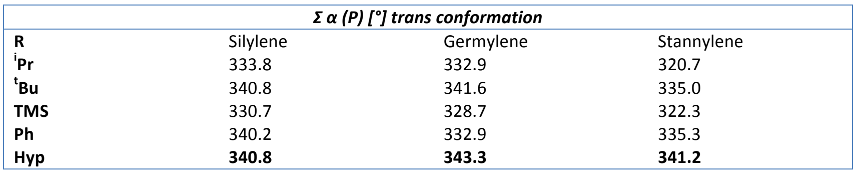
Conclusion and Outlook

The main targets of this work were an experimental and quantum chemical investigation α, α' P-stabilised tertylenes. The stabilising effect of various substituents should be determined. The assumption that the size of the atoms, the difference in electronegativities and the stronger pyramidalisation of the phosphorus atom counteract effective orbital overlap was explored within a DFT study. The chosen method/basis set (mPW1PW91/6-31+G* and M06L/IGLO-II for magnetic shildings) combinations were suitable for the calculations.

DPB proved to be an interesting starting material for the tetrylene synthesis, however so far no tetrylenes could be isolated. The calculations led to a noticeable amount of information about DBP derivatives and tetrylenes. The molecular modeling is very important for further synthesis and product analysis. The calculations led to a the result, that the TMS group as well as the Hyp group decrease the pyrimidalisation of the P-atom, which would be favoured for the tetrylene synthesis. The ^{t}Bu group did show similarities to the TMS group, which makes it a very promising candidate for the next steps in the synthesis. The other investigated substituents do not affect the bond lengths and angles significantly. There is an increase in the E-P bond lengths (Si$<$Ge$<$Sn) and a decrease (Si$>$Ge $>$Sn) of P-E-P bond angle moving down the group in the periodic table.
Another important information obtained by the DFT study, is the fact that with the tetrylenes there are always two conformers formed, which are very close

in energy. The *trans* conformation turned out to be more stable, due to a better orbital overlap and a smaller pyramidalisation of the phosphorus. (Fig.3.1)



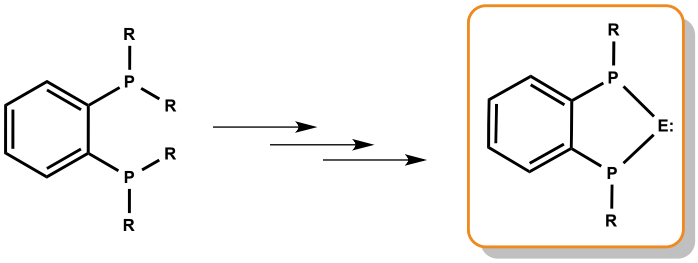


Σ α (P) [°] trans conformation			
R	Silylene	Germylene	Stannylene
^{i}Pr	333.8	332.9	320.7
^{t}Bu	340.8	341.6	335.0
TMS	330.7	328.7	322.3
Ph	340.2	332.9	335.3
Hyp	**340.8**	**343.3**	**341.2**

Figure 3.1.: Stabilisation *trans* conformation

For the tin compounds the colour of the reaction solution end even the crystals did fit to the calculation. However, so far no tetrylenes could be obtained. An interesting, anionic tin compound was isolated as side product. The investigation of three different pathways (A,B,C) for the formation of germylenes and stannylenes led to important information for subsequent reactions. The reaction pathway starting from bulky substituents on the phosphorus atom turned out to be more profitable. Therefore compound ***4*** (R = TMS) turned out to be an auspicious starting point for further synthesis. The performed synthesis yielded important information for continuing reactions and product isolation.

Initial trials using mixed-base systems of the type ^{n}BuLi-E(NMe$_2$)$_n$ led to crystals of an interesting byproduct. The unusual anion [Sn(NTMS$_2$)$_3$]$^-$ could be isolated, however the exact mechanism of this reaction is yet to be investigated. Nevertheless, this reaction pathway is promising, as the shifts predict a second product in solution, which is a phosphorus containing compound. An improvement of the reaction conditions should lead to better product isolation.



R = H, Me, TMS, Hyp, Phenyl
E = Si, Ge, Sn

R = TMS = *compound 5*

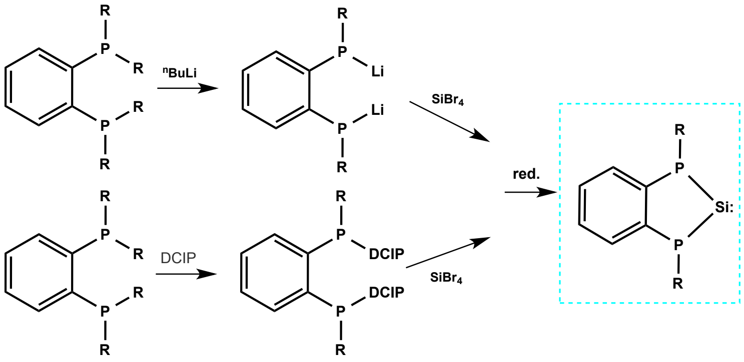
Figure 3.2.: Reaction scheme: profitable pathway

The germylene synthesis led to a crystal structure, which is not the expected germylene. However, a new product, a $Ge_2Li_2O_6Cl_2$ cage, could be isolated. This compound was also very sensitive in terms of air and temperature, which makes it difficult to handle. So far, only the $GeCl_2$·dioxane was used as reactant for the formation of germylene. A comparable reaction with an amide would also be conceivable.

3.0.3. Outlook

In the past few years the focus of attention was shifted to silylenes again. However no synthesis of silylenes was performed during this work. There are some promising ideas for reactions pathways which could lead to silylenes (Fig.3.3). The topic of 1,2-diphospasilylenes is rare in literature, which makes the investigation in such compounds interesting. The P-Si bond is regarded to be weak and a synthesis of stable derivatives is challenging.

For future product synthesis, it should be possible to produce similar precursors than ***4***, which would lead to other interesting, new compounds. As mentioned above there is a range of compounds, which also would be auspicious candidates for the synthesis. The improvement of the reaction pathways for the germylenes and stannylenes is an aim for subsequent reactions. An alternative method for the analysis for air and light sensitive crystals and the brown precipitate in case of the tin compounds has to be found.



DCIP: 2,6-dichlorophenol-indophenol (**Tillmans' reagent)**

R = H, Me, TMS, Hyp, Phenyl

Figure 3.3.: Possible reaction pathways silylenes

Chapter 4

Experimental Section

4.1. General Procedures

All reactions, unless otherwise stated, were carried out using standard Schlenk line techniques or in a dry box under nitrogen atmosphere. All solvents were dried and deoxygenated by a solvent drying system (Innovative Technology, Inc.). The compounds were stored under inert conditions at room temperature or reduced temperature.

4.1.1. Index of Chemicals

Table 4.1.: Chemicals

Chemical	CAS	M[g/mol]	ρ [g/mL]	Supplier
1,2- Bis(dimethoxyphosphoryl)benzene	15104-46-8	294.18	-	-
n-Butyllithium ^{n}BuLi	109-72-8	64.06	-	Sigma Aldrich 186171
1,2-Dichlorbenzene	195-50-1	147.00	1.3	Merck 102930
Germanium(II)-chloride·dioxane 1:1	28595-67-7	231.65	-	Sigma Aldrich 573515
Lithium aluminium hydride $LiAlH_4$	16853-85-3	37.95	0.92	In-house
Lithium bis(trimethylsilyl)amide	4039-32-1	167.33	0.891	Sigma Aldrich 225770
1,2-Diphosphinobenzene DPB	80510-04-9	142.08	-	ABCR AB130274
Trimethyl phosphate	512-56-1	140.08	-	Sigma Aldrich 241024
Trimethyl phosphite $P(OMe)_3$	121-45-9	124.08	1.052	Sigma Aldrich 240907
Trimethylsilyl chloride	75-77-4	108.64	0.854	Sigma Aldrich 386529
Tin(II)-chloride	7772-99-8	189.61	3.95	Fischer Chemical
Tin(II)-bromide	10031-24-0	278.52	5.12	Sigma Aldrich 309257

4.1.2. NMR

^{1}H (300.2 MHz), ^{13}C (75.5 MHz), ^{29}Si (59.6 MHz) and ^{31}P (121.5 MHz) NMR spectra were recorded on a Mercury 300 MHz spectrometer from Varian at 25℃. Chemical shifts are given in parts per million (ppm) relative to TMS (δ = 0 ppm) regarding ^{1}H, ^{13}C and ^{29}Si, ^{119}Sn relative to $SnMe_4$ and relative to 85% H_3PO_4 for ^{31}P. Coupling constants *(J)* are reported in Hertz (Hz). All NMR spectra were measured using a D_2O capillary as external lock signal.

4.1.3. X-ray Diffraction

All crystals suitable for single crystal X-ray diffractometry were removed from a Schlenk under inert conditions and immediately covered with a layer of silicone oil. A single crystal was selected, mounted on a glass rod on a copper pin, and placed in the cold N_2 stream provided by Bruker APEX2. For the solving the structure SHELXS97 (Sheldrick 2008) was used, to refine the structure SHELXL2014 (Sheldrick 2014) was used.

4.1.4. Computational details

All calculations have been carried out using the GAUSSIAN09 program package[37] on a computing cluster with blade architecture. For all calculations except calculations of NMR shieldings the mPW1PW91[19] hybrid functional was used. NMR shieldings were calculated using the M06L[38] pure functional as implemented in GAUSSIAN09. For optimisation and calculations of frequencies the 6-31+G* (backbone, silylenes) and SDD (germylenes, stannylenes) basis set was used. For calculation of NMR magnetic shieldings the all electron IGLO-II[39] basis set was used (σ ^{1}H = 32.8, σ ^{13}C = 186.6, σ ^{29}Si = 360.6 (TMS), σ ^{31}P = 624.7 (PH_3) and σ ^{119}Sn = 2721.3 ($Sn(Me)_4$)). The geometries of the molecules were were calculated in the gas phase, without the influence of a solvent. The optimised geometries of all discussed molecules are collected in Appendix A.

4.2. Synthesis

4.2.1. 1,2-Bis(dimethoxyphosphoryl)benzene *1*

According to literature[26] the photolysis of 1,2-dichlorobenzene in trimethylphosphite in a scale of 1:3.3 gives 1,2-bis(dimethoxyphosphoryl)benzene in 50% yield (reaction scheme Fig.4.1). The reaction time is at least 5 days and the reaction can be carried out on a multimolar scale.

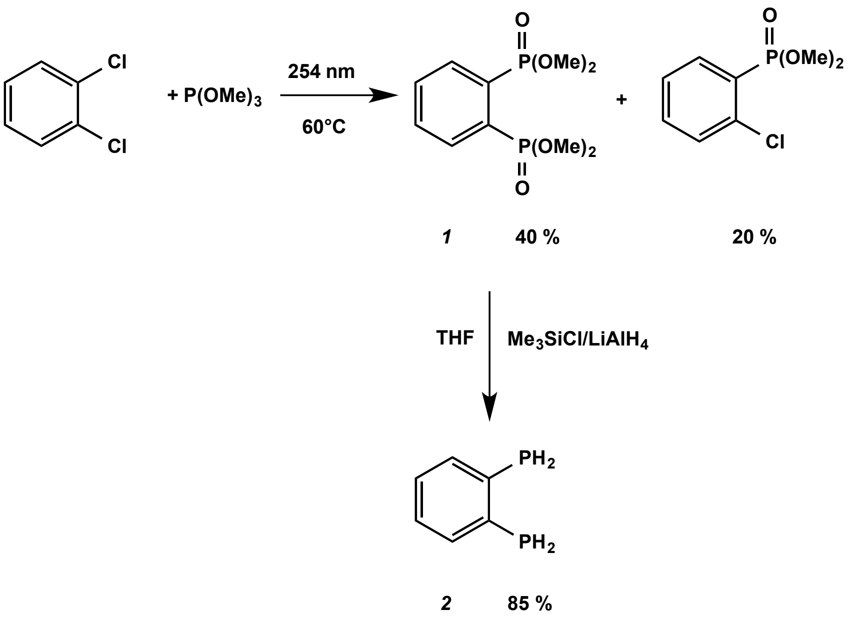


Figure 4.1.: Photolysis/Educt synthesis

A solution of 71.35 g (0.575 mol) trimethylphosphite and 26.09 g (0.178 mol) 1,2-dichlororobenzene was photolyzed at 60℃ for 7 days. An oily yellow suspension was formed. The residue was dissolved in acetone and cooled to -80℃ , which led to an immediate precipitation of a white powder. *(mp - 76 °C)*

To observe the reaction progress, NMR measurements of the reactions solution were performed using a D_2O capillary as external lock signal.
Yield: 27-30 %

^{13}C NMR (D_2O, 293 K): δ 54.07 ppm ($-CH_3$); δ 130.48 ppm (ring); δ 128.55 ppm (ring);
^{31}P NMR (D_2O, 293 K): δ 2.70 ppm

4.2.2. Synthesis of 1,2-Bis(phospino)benzene DPB *2*

Reaction of ***1*** with a trimethylsilyl chloride/lithium aluminium hydride mixture in a 1:1 ratio leads to production of *1,2-diphosphinobenzene* ***2***. No clean product could be isolated. Yield: 14-17 %

^{13}C NMR (D_2O, 293 K): δ 132.14 ppm; δ 130.36 ppm (ring); δ 127.77 ppm (ring);
^{31}P NMR (D_2O, 293 K): δ 73.34 (m) ppm

4.2.3. Synthesis of $C_6H_4(PHSiMe_3)_2$-1,2 *3*

A solution of ^nBuLi in hexanes (1.60 mol/L; 2.26 mL; 3.61 mmol) was added dropwise via syringe to a solution of DPB in n-hexane (10 wt%; 0.256 g; 1.81 mmol) in 10 mL THF at -30 ℃. The yellow solution was stirred at -30℃ for 40 minutes.

The mixture was cooled to -60℃ and TMS-Cl (ρ = 0.854 g/mol; 0.47 mL; 3.61 mmol) was added via syringe. The reaction solution is allowed to warm up to room temperature and stirred for 16 h (Fig.4.2). A white precipitate, lithium chloride, was formed. The product was filtered and the solvent was removed. The product of this step is a colourless to slightly yellow solution.
Yield: 80 - 85 %

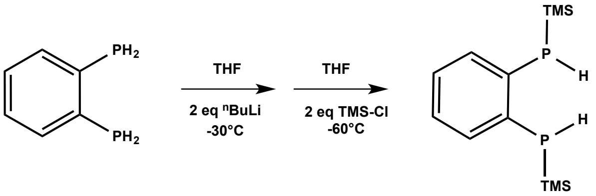


Figure 4.2.: Reaction scheme compound ***3***

^{29}Si NMR (D_2O, 293 K): δ 4.68 ppm (**Si**CH_3); δ 4.57 ppm ;
^{31}P NMR (D_2O, 293 K): δ -117.2 ppm (s,m separated by 9.34 ppm for mixture of *cis*/*trans* conformers

4.2.4. Synthesis of $C_6H_4(P(SiMe_3)_2)_2$-1,2 *4*

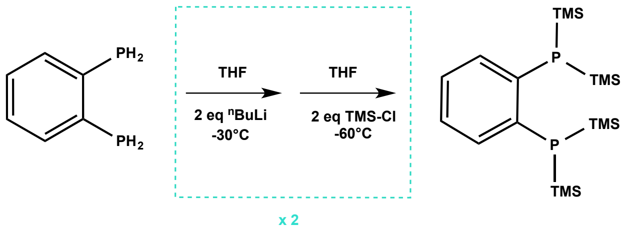


Figure 4.3.: Reaction scheme compound ***4***

To a solution of ***3*** (0.42 g; 1.48 mmol) in THF two equivalent of ^{n}BuLi in hexanes (1.60 mol/L; 1.85 mL; 2.96 mmol) were added via syringe at -30 ℃. The yellow solution was stirred at -30 ℃ for 40 minutes and was then cooled to -60 ℃. TMS-Cl (ρ = 0.854 g/mL; 0.38 mL; 2.96 mmol) was added dropwise via syringe. The solution was allowed to warm up to room temperature and was stirred for 16 h (Fig.4.3). The product is a slightly yellow, turbid solution due to the formed lithium chloride. The salts were removed by filtration. Through evaporation of the solvent the compound was concentrated. After a few days, crystals formed. Yield: 78 - 80 %

^{29}Si NMR (D_2O, 293 K): δ 2.79 ppm (**Si**CH3); δ 2.59 ppm; δ 2.29 ppm dupl.tripl.

^{31}P NMR (D_2O, 293 K): δ -140.4 ppm

4.2.5. Pretrials *germylene synthesis via* two different pathways

4.2.5.1. Pathway A

4.2.5.2. Synthesis of an germanium $Ge_2Li_2O_6Cl_2$ cage (compound *5*)

For this reaction germaniumdichloride·dioxane (0.669 g; 3.13 mmol) was dissolved in THF at room temperature and was then added dropwise to a solution of ***3*** (0.90g; 3.13 mmol) in THF at -50 ℃ via syringe. A colour change from yellow to orange occurs. The solution was stirred for 16 h at room temperature (Fig.4.4). The solution was concentrated and stored in the drybox fridge to form crystals. After the course of one week crystals formed, however in a quality not suitable for a X-ray measurement, recrystallisation was necessary. The crystals were separated from the mother liquor and redissolved in toluene. After the a week crystals with a quality good enough for a measurement were obtained.

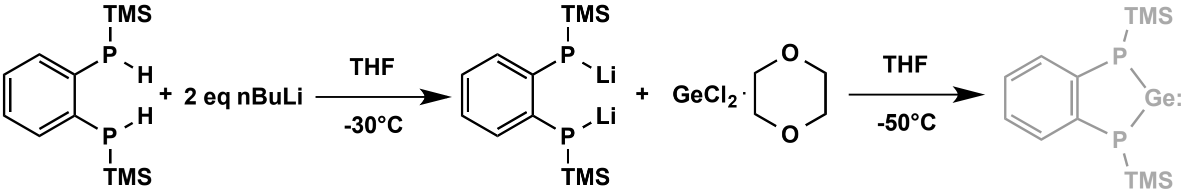


Figure 4.4.: Proposed reaction scheme pathway A/Germylene

NMR-data of the solution: ^{29}Si NMR (D_2O, 293 K): δ 21.87 ppm

^{31}P NMR (D_2O, 293 K): δ -45.3 ppm; δ -50.5 ppm

4.2.5.3. Pathway B

To a solution of ***4*** (0.64 g; 1.49 mmol) in DME (5 mL), KO^{t}Bu (2.1 eq; 0.31 g; 3.12 mmol) in 10 mL DME was added dropwise via syringe at RT. The solution turns red-orange and was further stirred for 16 h. (Fig.4.5) No clean product could be isolated.

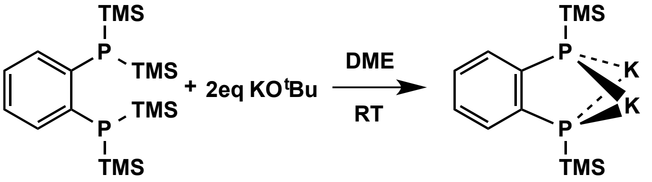


Figure 4.5.: General reaction scheme pathway B/Germylene

NMR-Data of this step: ^{29}Si NMR (D_2O, 293 K): δ 7.60 ppm; δ -6.99 ppm

^{31}P NMR (D_2O, 293 K): δ -99.53 ppm (P-K interaction -99.6 ppm[31]); δ -33.14 ppm; δ 7.52 ppm

4.2.6. Pretrials *stannylene synthesis via* three different pathways

4.2.6.1. Pathway A

Tin(II)chloride (0.38 g; 2.00 mmol) was dissolved in 5 mL THF at room temperature and was then added dropwise to a solution of ***3*** (0.37 g; 2 mmol) in 10 mL THF at -50℃ via syringe. A colour change from orange over red to brown occurs. The solution was stirred over night at room temperature.

The reaction solution turned black and a precipitate was formed. This is an indication that the reaction is sensitive to heat and light. It is advantageous to store the solution in the dark and under reduced temperature ($\leq$-30℃) which slows down the decomposition of the precipitate.

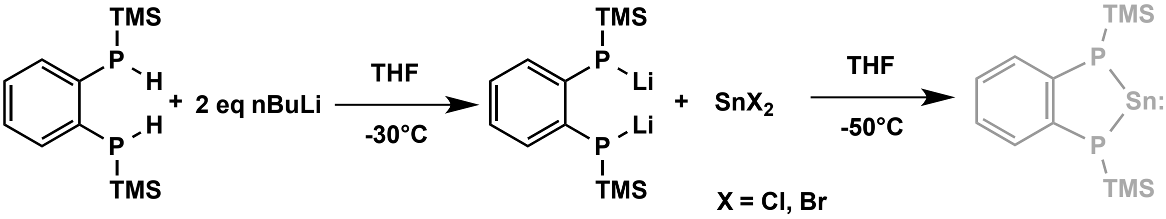


Figure 4.6.: Reaction scheme pathway A/Stannylene

NMR spectra of the cloudy red brown reaction solution were measured, while the precipitate formed again.

NMR Data of the solution: ^{29}Si NMR (D_2O, 293 K): δ 84.02 ppm
^{31}P NMR (D_2O, 293 K): δ 140.0 ppm
^{119}Sn NMR (D_2O, 293 K): δ 394.5 ppm; δ 378.9 ppm; δ -236.5 ppm

4.2.6.2. Pathway B

To a solution of ***4*** (1.34, 3.13 mmol) in DME (5 mL) KO^{t}Bu (0.74 g; 6.60 mmol) was dissolved in 10 mL DME and was added dropwise to the yellow solution via syringe. A bright red clear solution was obtained. For the next step a sus-

pension of tin(II)bromide (0.918 g; 3.13 mmol) in 10 mL THF was added slowly via syringe to the reaction solution at -50℃. The solution turns dark red. (Reaction scheme Fig.4.7).
After stirring over night a brown precipitate was formed. It was not possible to dissolve the precipitate in acetonitrile, THF, toluene or hexane.

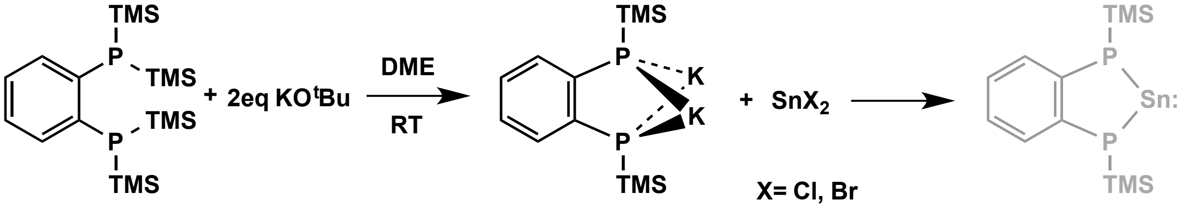


Figure 4.7.: General reaction scheme pathway B/Stannylene

NMR Data of solution (During the measurement, the precipitate formed again in the NMR tube.): ^{29}Si NMR (D_2O, 293 K): δ 7.60 ppm (^{t}BuOSiMe$_3$); δ 6.99 ppm
^{31}P NMR (D_2O, 293 K): δ -99.53 ppm (P-K interaction -99.6 ppm[31]); δ -33.14 ppm; δ 7.52 ppm

4.2.6.3. Pathway C

4.2.6.4. Formation of side product an anionic tin-compound *6*

An attempt was made to use TMEDA as a solvent as well as an reagent and perform a reaction with a mixed base system of the type ^{n}BuLi-E(NMe$_2$)$_n$.

Preparation of bis[N,N-bis(trimethylsilyl)amino]tinn(II)[35]

A solution of lithium bis(trimethylsilyl)amide (1 mol/L; 24 mL; 0.024 mol) in 30 mL THF was cooled to 0℃ with an ice bath and $SnCl_2$ (2.27 g; 0.012 mol) in 30 mL THF was added dropwise via syringe with intense stirring. The red-brown solution turned a bit brighter. After stirring over night at RT the product was concentrated by evaporating the solvent.
Yield: 86%

NMR-Data: ^{1}H NMR (D_2O, 293 K): δ 0.27 ppm
^{13}C NMR (D_2O, 293 K): δ 6.40 ppm
^{119}Sn NMR (D_2O, 293 K): δ 757.2 ppm

A solution of ***4*** (0.83 g; 1.805 mmol) in TMEDA (0.54 mL; 3,61 mmoL) and 5 mL hexane was prepared and cooled to 0℃. To this slightly yellow solution ^{n}BuLi in hexanes (1.60 mol/L; 2.25 mL; 3.61 mmol) was added dropwise via syringe. The solution was stirred for 30 minutes at 0℃. The solution was stored for 16 h at -80℃, which led to precipitation of a salt. The red-orange solution was filtered and stored at -80℃ for 16 h. Yellow crystals were formed.
The reaction solution was stored at 0℃ and Sn(NTMS)$_2$ was added dropwise via syringe (Fig.4.8). The solution turned dark red and was stored in the dark dry box at -30℃. Red crystals were formed after one night. The quality of the crystals was not good enough for X-ray measurement, therefore recrystallisation was necessary. The crystals were resolved in toluene and after the course of 24 h crystals formed. Due to high sensibility of the crystals to the exposure of light, it was quite difficult to measure them under ambient conditions.

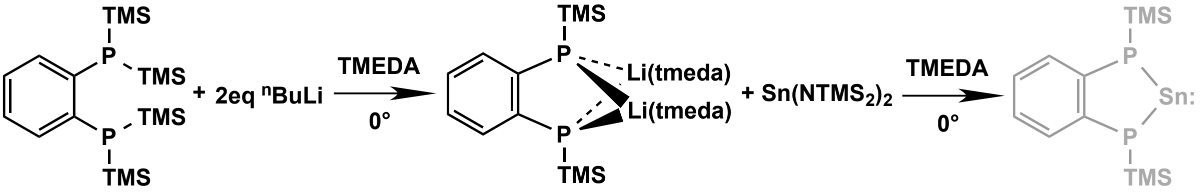


Figure 4.8.: General reaction scheme Pathway C/Stannylene

NMR-Data of solution: ^{13}C NMR (D_2O, 293 K): δ 116.70 ppm; δ 57.10 ppm; δ 45.80 ppm; δ 5.41 ppm
^{29}Si NMR (D_2O, 293 K): δ -1.74 ppm
^{31}P NMR (D_2O, 293 K): δ -36.80 ppm
^{119}Sn NMR (D_2O, 293 K): δ 770.80 ppm (reactant: (bis[N,N-bis(trimethylsilyl)amino]tinn(II)) δ ^{119}Sn = 757,16 ppm); δ 376.60 ppm

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Bibliography

[1] Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.*, **2009**, *109*(8), 3479.

[2] Diez-Gonzalez, S.; Nolan, S. P. *Coord. Chem. Rev.*, **2006**, *251*, 874.

[3] Eisler, D.; Less, R. J.; Naseri, V.; Rawson, J. M.; Wright, D. S. *Dalton Trans.*, **2008**, 2382.

[4] Yao, S.; Xiong, Y.; Driess, M. *Organometallics*, **2011**, *30*, 1748.

[5] Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Angew. Chem. Int. Ed.*, **2005**, *44*, 1700.

[6] du Mont, W. W.; Kroth, H. J. *Angew. Chem. Int. Ed. Engl.*, **1977**, *16*(792).

[7] Cowley, A. H.; Giolando, D. M.; Jones, R. A.; Nunn, C. M.; Power, J. M. *Polyhedron*, **1988**, *7(19-20)*(1909).

[8] Subblash, C.; Michael, G.; Chiang, Y.; Rauscher, D. J.; Buhro, W. E. *J. Am. Chem. Soc.*, **1993**, *115*, 160.

[9] Driess, M.; Janoschek, R.; Pritzkow, H.; Rell, S.; Winkler, U. *Angew. Chem. Int. Ed.*, **1995**, *14*, 1614.

[10] Kira, M.; Ishida, S.; Iwamoto, T.; Kabuto, C. *J. Am. Chem. Soc.*, **1999**, *121*(9722).

[11] Mueller, S.; Weinberger, G.; Schwarz, E.; Torvisco, A.; Dransfeld, A.; Fischer, R. C.; Hassler, K.; Flock, M. *Inorg. Chim. Acta*, **2014**, *423*, 517.

[12] Atkins, P. W.; de Paula, J. *Physikalische Chemie*. WILEY-VCH, 4 edition, **2006**.

[13] Cramer, C. J. *Essentials of Computational Chemistry - Theories and Models*, volume 1. Wiley, **2002**.

[14] Ostlund, N.; Szabo, A. *”Modern Quantum Chemistry”*. Dover Publications, **1996**.

[15] Levine, I. N. *Quantum Chemistry*. Pearson International Edition, 6 edition, **2009**.

[16] Hohenberg, P.; Kohn, W.; Sham, L. J. *Phys.Rev.*, **1964**.

[17] Nobelprize.org/Jan 2015.

[18] Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem.*, **2001**, *105*, 2936.

[19] Adamo, C.; Barone, V. *J. Phys. Chem.*, **1998**, *108*, 664.

[20] Ruud, K.; Helgaker, T.; Bak, K. L.; Jørgensen, P.; Jensen, H. J. A. *J. Chem. Phys.*, **1993**, *99*, 3847.

[21] Issleib, K.; Schmidt, H.; Bergmann, P. *Z. Anorg. Allg. Chem.*, **1985**, *529*(10), 216–221.

[22] Issleib, K.; Leissring, E.; Riemer, M. *Z. Anorg. Allg. Chem.*, **1984**, *519*(12), 75.

[23] Benson, S. *J. Chem. Educ.*, **1965**, *42*, 502.

[24] Hitchcock, P. B.; Lappert, M. F.; Leung, W.; Yin, P. *J. Chem. Soc. Dalton Trans.*, **1995**, 3925.

[25] http://www.chem.wisc.edu/areas/reich/handouts/nmr/p-data.htm Feb 2015.

[26] Kyba, E. P.; Liu, S. T.; Harris, R. L. *Organometallics*, **1983**, *2*(12), 1877.

[27] Khrustalev, V. N.; Antipin, M. Y.; Zemlyansky, N. N.; Borisova, I. V.; Ustynyuk, Y. A.; Lunin, V. V.; Barrau, J.; Rima, G. *J. Organomet. Chem.*, **2004**, 478.

[28] Weinert, C. S.; Fanwick, P. E.; Rothwell, I. P. *Dalton Trans.*, **2003**, 1795.

[29] Pugh, D.; Bloor, L. G.; Parkin, I. P.; Carmalt, C. J. *Chem. Eur. J.*, **2012**, *18*, 6079.

[30] Cappello, V.; Baumgartner, J.; Dransfeld, A.; Hassler, K. *Eur. J. Inorg. Chem.*, **2006**, 4589.

[31] Uhlig, F.; Uhlig, W. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1993**, *84*, 181.

[32] Müller, S. *Tetrylenes: An experimental and quantum chemical investigation an low-valent group 14 compounds and their precursors*. PhD thesis, Graz University of Technology, **2015**.

[33] Brochkarev, L.; Grachev, O. V.; F., Z. S. *J.Organomet.Chem.*, **1992**, *436*, 299.

[34] Grafov, A.; Vuorinen, A.; Repo, T.; Kemell, M.; Nieger, M.; Leskelä, M. *Eur. Polym. J.*, **2008**, *44*, 3797.

[35] Schaeffer, C. D. J.; Myers, L. K. *J. Chem. Educ.*, **1990**, *67*(4), 347.

[36] Chadwick, S. T.; Rennels, R. A.; L., R. J.; Collum, D. B. *J. Am. Chem. Soc.*, **2000**, *122*, 8640.

[37] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.; Izmaylov, A.; Bloino, J.; Zheng, G.; Sonnenberg, J.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.; Jr.; Peralta, J.; Ogliaro, F.; Bearpark, M.; Heyd, J.; Brothers, E.; Kudin, K.; Staroverov, V.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.; Iyengar, S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.; Klene, M.; Knox, J.; Cross, J.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.; Yazyev, O.; Austin, A.; Cammi, R.; Pomelli, C.; Ochterski, J.; Martin, R.; Morokuma, K.; Zakrzewski, V.; Voth, G.; Salvador, P.; Dannenberg, J.; Dapprich, S.; Daniels, A.; Farkas, Ö.; Foresman, J.; Ortiz, J.; Cioslowski, J.; Fox, D. *Gaussian Inc*, **2009**, *Revision A.1*.

[38] Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.*, **2006**, *125*, 1.

[39] Feller, D. *J. Comp. Chem.*, EMSL/Jan **1996**, *17*, 1571.

[40] Andriamizaka, J.; Coutet, C.; Escudie, J.; Satge, J. *Phosphorus, Sulfur Silicon Relat. Elem.*, **1991**, 341.

Appendix A

Optimised structures of investigated compounds.

A.0.7. Tetramethyl-1,2-phenylendiphosphonate

```
Tetramethyl-1,2-phenylendiphosphonate
Energy: -1524.66820359 a.u.
0 1
 C                  0.69038100   -3.64204000    0.07372200
 C                  1.37761400   -2.43275000    0.14164600
 C                  0.70307900   -1.20892100    0.06536000
 C                 -0.70311900   -1.20899600   -0.06547900
 C                 -1.37754600   -2.43287400   -0.14183400
 C                 -0.69020700   -3.64210600   -0.07395400
 H                  1.23889100   -4.57677300    0.13464400
 H                  2.45596800   -2.42147900    0.25997700
 H                 -2.45590500   -2.42168900   -0.26014200
 H                 -1.23862700   -4.57689000   -0.13490400
 P                 -1.82422000    0.21716100   -0.12721500
 P                  1.82413600    0.21729000    0.12717900
 O                 -3.17757400   -0.15612500   -0.61079000
 O                  3.17753800   -0.15609300    0.61057700
 O                 -1.14073800    1.40606200   -0.96587000
 O                 -1.73970300    0.78453700    1.36982300
 O                  1.73955800    0.78490500   -1.36976600
 O                  1.14081500    1.40610500    0.96609000
 C                 -2.54681700    1.91201500    1.72376500
 H                 -3.58962700    1.74177900    1.44489900
 H                 -2.46742100    2.01609700    2.80576300
 H                 -2.16798400    2.81285400    1.23447800
 C                  2.54717300    1.91204600   -1.72366500
 H                  3.58989600    1.74136400   -1.44475100
 H                  2.46785900    2.01617900   -2.80566400
 H                  2.16870300    2.81304200   -1.23438500
 C                 -1.31921400    1.44946100   -2.38412600
 H                 -1.00535500    2.44462200   -2.69969000
 H                 -0.68704300    0.69883500   -2.86568200
 H                 -2.36705200    1.28577300   -2.64493100
 C                  1.31891100    1.44878300    2.38442700
 H                  1.00501300    2.44380400    2.70039200
 H                  0.68657300    0.69794900    2.86543700
 H                  2.36667600    1.28493600    2.64542200
```

A.1. Structures of (1,2-Diphosphido)-benzenes

A.1.1. 1,2-Bis(phospino)benzene DPB

```
1,2-Bis(phospino)benzene DPB
Energy: -916.13062352

 C                  0.00763500    0.70682000    0.01550400
 C                 -0.00763500   -0.70682000    0.01550400
 C                  0.00825400   -1.38840100    1.24062300
 C                  0.00825400   -0.69665100    2.45214200
 C                 -0.00825400    0.69665100    2.45214200
 C                 -0.00825400    1.38840100    1.24062300
 H                  0.00885200   -2.47508900    1.24950300
 H                  0.01227500   -1.24680700    3.38932100
 H                 -0.01227500    1.24680700    3.38932100
 H                 -0.00885200    2.47508900    1.24950300
 P                  0.05829600   -1.62927700   -1.59683800
 H                  0.03609400   -2.93604100   -1.03507300
 H                 -1.33389700   -1.62837200   -1.90079400
 P                 -0.05829600    1.62927700   -1.59683800
 H                 -0.03609400    2.93604100   -1.03507300
 H                  1.33389700    1.62837200   -1.90079400
```

A.1.2. $C_6H_4(P(^iPr)_2)_2$-1,2

```
DPB(iPr)2
Energy: -1387.74911732

 C                  0.67649500    3.29135200    1.14236700
 C                  1.37656300    2.21625000    0.60473300
 C                  0.72523100    1.07186100    0.11747300
 C                 -0.69063800    1.02610500    0.19252800
 C                 -1.37649600    2.12253700    0.73254000
 C                 -0.71166500    3.24883700    1.20555400
 H                  1.21825800    4.15987900    1.50583800
 H                  2.45668800    2.28518100    0.56237400
 H                 -2.46093400    2.11131600    0.76842300
 H                 -1.27391800    4.08359700    1.61360200
 P                 -1.59538100   -0.46024000   -0.45494100
 P                  1.64427500   -0.28239800   -0.75871200
 C                 -2.20219600   -1.23782700    1.16242900
 C                 -2.51526200   -2.72239400    0.94864500
 C                 -3.33967400   -0.53701100    1.90171900
 H                 -1.30759300   -1.17977000    1.79708400
 H                 -1.68896600   -3.24370600    0.45596900
 H                 -2.70171300   -3.21395000    1.91109300
 H                 -3.40769500   -2.86602600    0.33144100
 H                 -3.09229500    0.49727600    2.15319000
 H                 -4.26613900   -0.53618300    1.31790500
 H                 -3.55235300   -1.05898100    2.84298000
 C                 -3.11192800    0.31551500   -1.24116100
 C                 -4.05812300   -0.77738600   -1.74377300
 C                 -2.66713200    1.20438500   -2.40520500
 H                 -3.65403900    0.93162300   -0.51245600
 H                 -4.47679900   -1.37608200   -0.93039600
 H                 -4.89851400   -0.32693500   -2.28536800
 H                 -3.54416100   -1.45743600   -2.43195600
 H                 -2.02204800    2.02390500   -2.07684400
```

H	-2.11504700	0.62242400	-3.15132600
H	-3.54182000	1.64157600	-2.90150400
C	3.41517100	0.36575800	-0.85678300
C	4.12079400	-0.33986900	-2.02303200
C	4.31426800	0.35713200	0.38138500
H	3.26786200	1.40781700	-1.17210500
H	3.53472900	-0.27695400	-2.94406800
H	5.09923300	0.12001100	-2.20816800
H	4.29270900	-1.40016300	-1.81135000
H	3.85353900	0.82577700	1.25417600
H	4.58858400	-0.66424000	0.66175200
H	5.24842600	0.89243700	0.16876800
C	1.60768400	-1.67660900	0.51216900
C	1.85762500	-1.33786400	1.98094300
C	2.46759300	-2.85416100	0.04701600
H	0.56235900	-2.00035800	0.42076000
H	1.26980000	-0.47502400	2.30802700
H	1.57725600	-2.19182400	2.61131200
H	2.90970300	-1.12037100	2.18084000
H	2.26092400	-3.12005000	-0.99449100
H	3.53680400	-2.63850900	0.13653800
H	2.26389500	-3.73634900	0.66545600

A.1.3. $C_6H_4(P(^tBu)_2)_2$-1,2

DPB(tBu)2
Energy: -1544.94962645

C	0.69421600	0.03634600	-3.43482400
C	1.37286900	0.06290300	-2.22215600
C	0.71020700	0.02384800	-0.98499200
C	-0.71023400	-0.02328200	-0.98501300
C	-1.37289000	-0.06147700	-2.22220900
C	-0.69422900	-0.03410600	-3.43485400
H	1.24776300	0.06833900	-4.36884900
H	2.45411300	0.11546900	-2.23953700
H	-2.45413800	-0.11397300	-2.23963000
H	-1.24776800	-0.06543300	-4.36890600
P	1.66974200	-0.04775700	0.61563500
C	-2.35935200	-1.73074700	0.76332900
C	-3.32284100	-1.77350900	1.95602900
C	-3.03161400	-2.34198100	-0.46922800
C	-1.13859700	-2.59427100	1.10995500
H	-2.87585000	-1.33113200	2.85263800
H	-4.26472300	-1.25734600	1.75257000
H	-3.56932100	-2.81778700	2.18702700
H	-2.34934700	-2.37843500	-1.32296700
H	-3.32403800	-3.37656100	-0.24281300
H	-3.93527900	-1.80989000	-0.77389300
H	-1.46480100	-3.61967700	1.32899300
H	-0.44021200	-2.64196400	0.27046600
H	-0.59845000	-2.20913400	1.97962800
C	3.12508200	-1.26890500	0.29022900
C	4.37606100	-0.79029600	-0.45441900
C	3.55688000	-1.72522300	1.69662700
C	2.55937700	-2.49844300	-0.43164900
H	4.17473600	-0.47569100	-1.48109100
H	4.87928000	0.03181200	0.06030800
H	5.09472600	-1.61929500	-0.51136800
H	2.71470200	-2.14438300	2.25506200

H	4.32927600	-2.50086600	1.61084900
H	3.97589900	-0.90861700	2.29074300
H	3.32442700	-3.28531900	-0.45687100
H	1.68938900	-2.90600900	0.09092600
H	2.26514600	-2.28407000	-1.46190700
C	2.35941900	1.73027300	0.76422000
C	1.13870700	2.59370800	1.11117200
C	3.32284300	1.77239500	1.95699900
C	3.03180400	2.34200500	-0.46801800
H	0.44034500	2.64176100	0.27168800
H	0.59853000	2.20823600	1.98067900
H	1.46495300	3.61901100	1.33063200
H	4.26473600	1.25634900	1.75329200
H	3.56931500	2.81654600	2.18857700
H	2.87581900	1.32953100	2.85335000
H	3.32424200	3.37648200	-0.24114900
H	3.93547400	1.81000100	-0.77282700
H	2.34960700	2.37882300	-1.32180000
P	-1.66978100	0.04740600	0.61564100
C	-3.12513800	1.26870600	0.29089100
C	-2.55947300	2.49868500	-0.43025800
C	-4.37607900	0.79050400	-0.45407500
C	-3.55697600	1.72417100	1.69755100
H	-1.68954600	2.90602300	0.09259700
H	-2.26516000	2.28491000	-1.46061800
H	-3.32457700	3.28552100	-0.45508900
H	-4.87942400	-0.03176900	0.06026000
H	-5.09466900	1.61958800	-0.51075300
H	-4.17466000	0.47631900	-1.48086000
H	-4.32936700	2.49986900	1.61223100
H	-3.97600800	0.90720500	2.29116700
H	-2.71480900	2.14298800	2.25626100

A.1.4. $C_6H_4(P(Ph)_2)_2$-1,2

DPB(Ph)2
Energy:-1840.11699208

C	-0.68669800	0.08536000	3.52849200
C	-1.37399400	0.17792100	2.31910800
C	-0.70109200	0.08000900	1.09769900
C	0.70252100	-0.08325300	1.09641000
C	1.37677700	-0.19098600	2.31623400
C	0.69019800	-0.10905600	3.52672100
H	-1.23068600	0.15868300	4.46563000
H	-2.44962700	0.32423200	2.32730400
H	2.45266900	-0.33532900	2.32323700
H	1.23529800	-0.19013600	4.46266300
P	1.56907600	-0.18925600	-0.53890000
P	-1.56590800	0.19341300	-0.53611600
C	-3.21619600	0.85663400	-0.04996000
C	-4.33616000	0.06771700	0.23712800
C	-3.35119200	2.25160900	-0.01502900
C	-5.55587200	0.65937200	0.56280600
H	-4.25812500	-1.01478700	0.20281600
C	-4.56481500	2.84260600	0.32440800
H	-2.49716900	2.87792800	-0.26146800
C	-5.67261800	2.04655000	0.61276900
H	-6.41604300	0.03239000	0.77944400
H	-4.64916700	3.92505800	0.35082100

H	-6.62343900	2.50591300	0.86588200
C	-1.94217900	-1.57349100	-0.89469400
C	-2.30491100	-1.88605100	-2.21142000
C	-1.86688200	-2.60818800	0.04392400
C	-2.60742000	-3.19516700	-2.57612600
H	-2.34457700	-1.09661400	-2.95762500
C	-2.15699900	-3.92129300	-0.32329400
H	-1.57888300	-2.38980300	1.06778500
C	-2.53170800	-4.21770800	-1.63192500
H	-2.89004900	-3.41835200	-3.60068700
H	-2.09144600	-4.71346100	0.41710900
H	-2.75806200	-5.24097900	-1.91642200
C	3.21657500	-0.85884000	-0.05126700
C	4.34137900	-0.07216300	0.22160900
C	3.34562200	-2.25408100	-0.00498700
C	5.56116500	-0.66612200	0.54329500
H	4.26624100	1.01039700	0.18206400
C	4.55900700	-2.84708200	0.33150400
H	2.48753500	-2.87931300	-0.23985200
C	5.67255300	-2.05314800	0.60425300
H	6.42562800	-0.04088400	0.74758900
H	4.63885400	-3.92955800	0.36859900
H	6.62312100	-2.51449800	0.85466900
C	1.94831100	1.57920100	-0.88867200
C	2.31773900	1.90084200	-2.20147200
C	1.85975700	2.60882500	0.05431200
C	2.61122900	3.21399900	-2.55820200
H	2.37063100	1.11500500	-2.95076600
C	2.14080100	3.92609200	-0.30510400
H	1.57166200	2.38261000	1.07620800
C	2.51957600	4.23196000	-1.61013000
H	2.89951100	3.44402100	-3.57966600
H	2.06487600	4.71407300	0.43880500
H	2.73688200	5.25865700	-1.88923600

A.1.5. $C_6H_4(P(SiMe_3)_2)_2$-1,2

C6H4[P(SiMe3)2]-1,2
Energy: -2550.70376012
0 1

C	0.69552500	-0.02281200	3.50650800
C	1.37855700	-0.03361900	2.29501000
C	0.70823000	-0.00397800	1.06268500
C	-0.70813400	0.00333500	1.06274700
C	-1.37832900	0.03267900	2.29514700
C	-0.69517200	0.02159600	3.50657800
H	1.24790200	-0.04761000	4.44132600
H	2.46248800	-0.07695800	2.30492400
H	-2.46224800	0.07599800	2.30519100
H	-1.24745800	0.04619100	4.44145600
P	1.63299500	0.09618900	-0.54599500
P	-1.63296600	-0.09631200	-0.54593200
Si	-2.36181500	2.03642500	-0.82873200
Si	-3.48369300	-1.34302100	-0.09176000
Si	3.48326700	1.34333700	-0.09141600
Si	2.36220200	-2.03635500	-0.82915800
C	2.92551400	2.89379500	0.83216200
H	2.19032300	3.45623400	0.24824300
H	2.47741100	2.66257700	1.80306400
H	3.78582600	3.55116100	1.00656300
C	4.91659500	0.54858900	0.86183900

```
 H                  5.73313200    1.27653200    0.94770300
 H                  4.64523600    0.24206200    1.87660500
 H                  5.31441400   -0.32849200    0.34171800
 C                  4.14170200    1.85156800   -1.78831100
 H                  4.99904800    2.52584800   -1.67564400
 H                  4.47156000    0.99213000   -2.38038200
 H                  3.37254000    2.37602200   -2.36400800
 C                 -2.92636900   -2.89392000    0.83137200
 H                 -3.78725300   -3.55013100    1.00730500
 H                 -2.19283600   -3.45743800    0.24640400
 H                 -2.47647400   -2.66296700    1.80149800
 C                 -4.91669100   -0.54817000    0.86191700
 H                 -5.73356500   -1.27579300    0.94734500
 H                 -4.64521900   -0.24239300    1.87687700
 H                 -5.31411600    0.32943100    0.34237300
 C                 -4.14248500   -1.85069100   -1.78867500
 H                 -4.47372900   -0.99124200   -2.37994200
 H                 -3.37309900   -2.37390800   -2.36518700
 H                 -4.99897300   -2.52603700   -1.67586200
 C                 -3.66772200    2.02156200   -2.19522900
 H                 -4.59022300    1.51887200   -1.88866200
 H                 -3.92948200    3.05125800   -2.46638900
 H                 -3.29515000    1.52556800   -3.09739300
 C                 -3.06979900    2.83811900    0.72820800
 H                 -3.32371900    3.88525500    0.52199400
 H                 -3.97631100    2.33748600    1.08068600
 H                 -2.34019700    2.82822400    1.54418100
 C                 -0.88687700    3.06044000   -1.40295600
 H                 -1.20127900    4.08579000   -1.63273700
 H                 -0.11689400    3.10988900   -0.62732700
 H                 -0.42673700    2.62928000   -2.29683900
 C                  3.66745200   -2.02095400   -2.19628000
 H                  3.92973500   -3.05044900   -2.46765200
 H                  3.29426200   -1.52505000   -3.09823800
 H                  4.58976600   -1.51772400   -1.88997100
 C                  0.88712300   -3.06063700   -1.40253100
 H                  0.11757300   -3.11023400   -0.62648300
 H                  0.42647400   -2.62961300   -2.29620900
 H                  1.20163900   -4.08593500   -1.63241900
 C                  3.07108800   -2.83801900    0.72739500
 H                  2.34171500   -2.82846300    1.54358000
 H                  3.32522400   -3.88505400    0.52094100
 H                  3.97755200   -2.33719400    1.07967700
```

A.2. Silylene

A.2.0.1. $C_6H_4(P^iPr)_2Si$ *cis*

```
C6H4P(iPr)2Si cis
Energy: -1440.21209682
 C                  1.05638800   -0.12406600   -0.70903900
 C                  1.05638800   -0.12406600    0.70903900
 C                  2.25599200    0.11259400    1.39458500
 C                  3.42705300    0.38593000    0.69829500
 C                  3.42705300    0.38593000   -0.69829500
 C                  2.25599200    0.11259400   -1.39458500
 H                  2.27426200    0.09914200    2.47995800
 H                  4.34226800    0.59554800    1.24352100
```

```
 H                  4.34226800    0.59554800   -1.24352100
 H                  2.27426200    0.09914200   -2.47995800
 Si                -2.11005100   -0.08907000    0.00000000
 P                 -0.52577200   -0.52095300    1.49114200
 P                 -0.52577200   -0.52095300   -1.49114200
 C                 -0.64595700    0.36266600    3.13835000
 C                 -0.11199900   -0.52098600    4.26869200
 C                 -2.08626700    0.78919000    3.41891700
 H                 -0.01915400    1.25806800    3.04843000
 H                  0.91371100   -0.85546600    4.09024100
 H                 -0.12540900    0.03026500    5.21668500
 H                 -0.73283800   -1.41494100    4.38641200
 H                 -2.44154400    1.53165200    2.69921300
 H                 -2.77096300   -0.06531900    3.38644400
 H                 -2.15464600    1.22686300    4.42141000
 C                 -0.64595700    0.36266600   -3.13835000
 C                 -2.08626700    0.78919000   -3.41891700
 C                 -0.11199900   -0.52098600   -4.26869200
 H                 -0.01915400    1.25806800   -3.04843000
 H                 -2.44154400    1.53165200   -2.69921300
 H                 -2.15464600    1.22686300   -4.42141000
 H                 -2.77096300   -0.06531900   -3.38644400
 H                  0.91371100   -0.85546600   -4.09024100
 H                 -0.73283800   -1.41494100   -4.38641200
 H                 -0.12540900    0.03026500   -5.21668500
```

A.2.0.2. $C_6H_4(P^iPr)_2Si$ *trans*

```
C6H4P(iPr)2Si trans
Energy: -1440.20936236
 C                 -0.58210300    3.48278400   -0.01338300
 C                 -1.29130800    2.29067300    0.06529000
 C                 -0.62096400    1.06700000   -0.06653200
 C                  0.77038700    1.03500900   -0.29864200
 C                  1.45789700    2.25114100   -0.40641400
 C                  0.79455700    3.46318700   -0.24467000
 H                 -1.10387000    4.42905200    0.09298900
 H                 -2.36431200    2.31539700    0.22923000
 H                  2.51554700    2.25300900   -0.64915200
 H                  1.34667300    4.39479300   -0.32226900
 Si                -0.05595200   -2.18201900   -0.41564600
 P                 -1.37682900   -0.55790900    0.04727400
 P                  1.54732100   -0.58087900   -0.68860700
 C                 -3.23075800   -0.48657400   -0.02999400
 C                 -3.83747600   -0.13885900    1.33289500
 C                 -3.78003900   -1.80993700   -0.56272300
 H                 -3.46981400    0.30901400   -0.74754500
 H                 -3.43764700    0.79246400    1.74364800
 H                 -4.92454400   -0.02798700    1.24226200
 H                 -3.63730900   -0.93342900    2.05849600
 H                 -3.42073900   -2.02110700   -1.57306800
 H                 -3.49104900   -2.64794800    0.08024100
 H                 -4.87478300   -1.77303900   -0.58662600
 C                  2.83624400   -0.92429000    0.65320200
 C                  3.93990300    0.13054000    0.68256300
 C                  3.42733000   -2.31307400    0.40632300
 H                  2.32244700   -0.91947900    1.62110700
 H                  3.56288200    1.11088100    0.98241100
 H                  4.70681400   -0.16093700    1.41043700
 H                  4.42682200    0.22782800   -0.29435200
 H                  2.66752000   -3.09984300    0.43604100
```

```
 H                   3.92557600   -2.36227400   -0.56799000
 H                   4.17373400   -2.54191600    1.17568000
```

A.2.0.3. $C_6H_4(P^tBu)_2Si$ *cis*

```
C6H4P(tBu)2Si cis
Energy: -1518.82233836
 C                  -1.11098500   -0.29670900    0.71047200
 C                  -1.11098500   -0.29670900   -0.71047200
 C                  -2.32627400   -0.12039500   -1.39028000
 C                  -3.50782500    0.10720200   -0.69796300
 C                  -3.50782500    0.10720200    0.69796300
 C                  -2.32627400   -0.12039500    1.39028000
 H                  -2.35175500   -0.15502500   -2.47365700
 H                  -4.43114600    0.27033400   -1.24538400
 H                  -4.43114600    0.27033400    1.24538400
 H                  -2.35175500   -0.15502500    2.47365700
 P                   0.47126900   -0.69456800    1.50399700
 P                   0.47126900   -0.69456800   -1.50399700
 Si                  2.05682500   -0.33717600    0.00000000
 C                   0.27992100    1.69628700    3.02510100
 C                  -0.02541000   -0.47916600    4.26048400
 C                   2.22972100    0.17540700    3.43719100
 H                   0.85117700    2.23055100    2.26024900
 H                  -0.78030000    1.78466000    2.77351000
 H                   0.43923200    2.20256600    3.98646500
 H                   0.29266000   -1.52173200    4.35225300
 H                   0.17913400    0.02497000    5.21353500
 H                  -1.10845000   -0.47104900    4.11426300
 H                   2.41125100    0.60595400    4.42958300
 H                   2.60372000   -0.85365000    3.44678600
 H                   2.82025600    0.74393400    2.71285900
 C                  -0.02541000   -0.47916600   -4.26048400
 C                   0.27992100    1.69628700   -3.02510100
 C                   2.22972100    0.17540700   -3.43719100
 H                   0.29266000   -1.52173200   -4.35225300
 H                  -1.10845000   -0.47104900   -4.11426300
 H                   0.17913400    0.02497000   -5.21353500
 H                   0.85117700    2.23055100   -2.26024900
 H                   0.43923200    2.20256600   -3.98646500
 H                  -0.78030000    1.78466000   -2.77351000
 H                   2.41125100    0.60595400   -4.42958300
 H                   2.82025600    0.74393400   -2.71285900
 H                   2.60372000   -0.85365000   -3.44678600
 C                   0.72875300    0.23691400    3.13123700
 C                   0.72875300    0.23691400   -3.13123700
```

A.2.0.4. $C_6H_4(P^tBu)_2Si$ *trans*

```
C6H4P(tBu)2Si trans
Energy: -1518.81854777
 C                  -0.67042100    3.50895900    0.15710100
 C                  -1.34453600    2.30363700    0.30035200
 C                  -0.67414100    1.08338200    0.12817200
 C                   0.69918200    1.08723300   -0.20331300
 C                   1.36419700    2.31449400   -0.34128000
```

```
 C                  0.69029600    3.51442900   -0.15528400
 H                 -1.20369200    4.44472500    0.29413400
 H                 -2.39534800    2.31656500    0.56675800
 H                  2.41239300    2.33703900   -0.61740100
 H                  1.22246500    4.45454700   -0.26366700
 P                 -1.38612300   -0.55042800    0.45406400
 P                  1.43392600   -0.52821800   -0.59932600
 Si                 0.01061200   -2.14791000   -0.09116300
 C                 -4.09483400   -0.04049300    1.02074200
 C                 -3.44269100   -0.04988300   -1.41634000
 C                 -3.52133500   -2.18542800   -0.10719600
 H                 -3.94002800   -0.49802400    2.00238700
 H                 -3.92273900    1.03400100    1.12122800
 H                 -5.14780000   -0.17764100    0.74414400
 H                 -2.83356100   -0.52854400   -2.18848500
 H                 -4.49882500   -0.16618000   -1.69270300
 H                 -3.21247500    1.01896300   -1.42143400
 H                 -4.59166600   -2.31431700   -0.30938700
 H                 -2.96405100   -2.68898500   -0.90199700
 H                 -3.29804900   -2.69144700    0.83801700
 C                  4.19408200    0.01463000   -0.77668700
 C                  3.23891800   -0.14895100    1.54861600
 C                  3.50316300   -2.19780800    0.12634500
 H                  4.15776800   -0.36460100   -1.80230900
 H                  4.03851400    1.09563000   -0.81091900
 H                  5.20574100   -0.15513800   -0.38689400
 H                  2.53380400   -0.66777300    2.20450300
 H                  4.25004100   -0.28843700    1.95355500
 H                  3.00888300    0.91960000    1.58570400
 H                  4.54540100   -2.33722600    0.43884200
 H                  2.86634500   -2.75340100    0.82041100
 H                  3.39247000   -2.64360500   -0.86798700
 C                 -3.19938500   -0.68719500   -0.04561900
 C                  3.17563900   -0.69955800    0.12251100
```

A.2.0.5. $C_6H_4(PSiMe_3)_2Si$ *cis*

```
[C6H4P(Si(SiMe3)3)2Si] cis
Energy: -2021.70230445

 0 1
 C                 -1.33216200   -0.50975900    0.70722000
 C                 -1.33216200   -0.50975900   -0.70722000
 C                 -2.51238400   -0.18275200   -1.39178900
 C                 -3.65859300    0.18453400   -0.69823400
 C                 -3.65859300    0.18453400    0.69823400
 C                 -2.51238400   -0.18275200    1.39178900
 H                 -2.53388100   -0.22059700   -2.47654800
 H                 -4.55738200    0.45475300   -1.24428000
 H                 -4.55738200    0.45475300    1.24428000
 H                 -2.53388100   -0.22059700    2.47654800
 P                  0.18062000   -1.07238000    1.55023400
 P                  0.18062000   -1.07238000   -1.55023400
 Si                 1.77269700   -1.09003400    0.00000000
 C                  0.75988000    2.16320800    2.53950700
 C                 -0.40374200    0.23033300    4.64163800
 C                  2.50707700   -0.13357100    3.70342200
 H                  1.51614200    2.30631800    1.76138800
 H                 -0.21416500    2.41953600    2.11072900
 H                  0.96767000    2.87106900    3.35096600
 H                 -0.49253700   -0.80900600    4.97263400
```

```
 H                  -0.02652900    0.82139100    5.48503800
 H                  -1.40653900    0.60085100    4.40774400
 H                   2.85229400    0.50016700    4.52880200
 H                   2.52231200   -1.17166700    4.05003700
 H                   3.22842300   -0.04234300    2.88563800
 C                  -0.40374200    0.23033300   -4.64163800
 C                   0.75988000    2.16320800   -2.53950700
 C                   2.50707700   -0.13357100   -3.70342200
 H                  -0.49253700   -0.80900600   -4.97263400
 H                  -1.40653900    0.60085100   -4.40774400
 H                  -0.02652900    0.82139100   -5.48503800
 H                   1.51614200    2.30631800   -1.76138800
 H                   0.96767000    2.87106900   -3.35096600
 H                  -0.21416500    2.41953600   -2.11072900
 H                   2.85229400    0.50016700   -4.52880200
 H                   3.22842300   -0.04234300   -2.88563800
 H                   2.52231200   -1.17166700   -4.05003700
 Si                  0.77611200    0.39096500    3.17844700
 Si                  0.77611200    0.39096500   -3.17844700
```

A.2.0.6. $C_6H_4(PSiMe_3)_2Si$ *trans*

```
C6H4P(SiMe3)2 Si trans
Energy: -2021.70053726

 C                  -1.33216200   -0.50975900    0.70722000
 C                  -1.33216200   -0.50975900   -0.70722000
 C                  -2.51238400   -0.18275200   -1.39178900
 C                  -3.65859300    0.18453400   -0.69823400
 C                  -3.65859300    0.18453400    0.69823400
 C                  -2.51238400   -0.18275200    1.39178900
 H                  -2.53388100   -0.22059700   -2.47654800
 H                  -4.55738200    0.45475300   -1.24428000
 H                  -4.55738200    0.45475300    1.24428000
 H                  -2.53388100   -0.22059700    2.47654800
 P                   0.18062000   -1.07238000    1.55023400
 P                   0.18062000   -1.07238000   -1.55023400
 Si                  1.77269700   -1.09003400    0.00000000
 C                   0.75988000    2.16320800    2.53950700
 C                  -0.40374200    0.23033300    4.64163800
 C                   2.50707700   -0.13357100    3.70342200
 H                   1.51614200    2.30631800    1.76138800
 H                  -0.21416500    2.41953600    2.11072900
 H                   0.96767000    2.87106900    3.35096600
 H                  -0.49253700   -0.80900600    4.97263400
 H                  -0.02652900    0.82139100    5.48503800
 H                  -1.40653900    0.60085100    4.40774400
 H                   2.85229400    0.50016700    4.52880200
 H                   2.52231200   -1.17166700    4.05003700
 H                   3.22842300   -0.04234300    2.88563800
 C                  -0.40374200    0.23033300   -4.64163800
 C                   0.75988000    2.16320800   -2.53950700
 C                   2.50707700   -0.13357100   -3.70342200
 H                  -0.49253700   -0.80900600   -4.97263400
 H                  -1.40653900    0.60085100   -4.40774400
 H                  -0.02652900    0.82139100   -5.48503800
 H                   1.51614200    2.30631800   -1.76138800
 H                   0.96767000    2.87106900   -3.35096600
 H                  -0.21416500    2.41953600   -2.11072900
 H                   2.85229400    0.50016700   -4.52880200
 H                   3.22842300   -0.04234300   -2.88563800
 H                   2.52231200   -1.17166700   -4.05003700
```

Si	0.77611200	0.39096500	3.17844700
Si	0.77611200	0.39096500	-3.17844700

A.2.0.7. $C_6H_4(Ph)_2Si$ *cis*

[C6H4P(Ph)2Sn] cis
Energy: -7401.9394578

C	-0.72636200	1.25004000	-0.59747200
C	0.68672700	1.23499800	-0.54146700
C	1.38223400	2.41904200	-0.25785400
C	0.68766100	3.59026900	0.01427000
C	-0.70945900	3.60639600	-0.03425700
C	-1.40888200	2.45166100	-0.36065500
H	2.46811100	2.41591000	-0.23719600
H	1.23408300	4.49624300	0.25831800
H	-1.25059300	4.52437200	0.17379300
H	-2.49348500	2.47352200	-0.41704800
P	-1.54021900	-0.27431600	-1.16062600
P	1.46603400	-0.32963600	-1.00674900
Si	-0.05314900	-1.92519100	-0.79163600
C	-3.01525000	-0.53996200	-0.11018200
C	-4.11851500	-1.19475600	-0.67189300
C	-3.07652800	-0.13519300	1.23007400
C	-5.25354000	-1.45292800	0.09361000
H	-4.08956900	-1.49644800	-1.71498300
C	-4.21999500	-0.37647400	1.98606800
H	-2.22843400	0.37203900	1.67981500
C	-5.30909200	-1.04059500	1.42268200
H	-6.09964000	-1.96495600	-0.35468600
H	-4.25566000	-0.05434900	3.02267400
H	-6.19718100	-1.23269200	2.01690400
C	3.01745200	-0.56040900	-0.07982300
C	4.08355400	-1.21734700	-0.70697300
C	3.17023300	-0.12343200	1.24316700
C	5.27410300	-1.44572900	-0.02057500
H	3.98092500	-1.54581100	-1.73701400
C	4.36814100	-0.33618200	1.91860800
H	2.34921100	0.38003000	1.74404400
C	5.42102600	-1.00147200	1.29103400
H	6.09095300	-1.96039800	-0.51728500
H	4.47505300	0.00811400	2.94298000
H	6.35204900	-1.17118000	1.82305500

A.2.0.8. $C_6H_4(Ph)_2Si$ *trans*

[C6H4P(Ph)2Sn] trans
Energy: -7401.9381944

C	-0.66981400	3.54349700	0.20202600
C	-1.33603400	2.34377000	0.41708200
C	-0.66952100	1.12727800	0.21743200
C	0.66938800	1.12743200	-0.21731700
C	1.33564100	2.34403400	-0.41712400
C	0.66914400	3.54363500	-0.20222900
H	-1.18971700	4.48374900	0.35840600

H	-2.36910900	2.34764700	0.75239700
H	2.36871000	2.34808200	-0.75245400
H	1.18882200	4.48398800	-0.35873700
P	-1.34053400	-0.49246100	0.66192800
P	1.34057200	-0.49225900	-0.66159800
Si	0.00021500	-2.12513400	0.00010800
C	-3.10977200	-0.55382600	0.23249500
C	-3.98307500	-1.25818700	1.07065700
C	-3.61953500	0.05991900	-0.92016600
C	-5.33666100	-1.35846800	0.75674500
H	-3.60162000	-1.72505800	1.97412200
C	-4.97524400	-0.02758800	-1.22076100
H	-2.95305500	0.60185100	-1.58403500
C	-5.83651600	-0.74010000	-0.38650200
H	-6.00149000	-1.91169900	1.41313000
H	-5.35831700	0.45315000	-2.11600500
H	-6.89276800	-0.81103900	-0.62727400
C	3.10987200	-0.55362200	-0.23248700
C	3.98295300	-1.25851000	-1.07043600
C	3.61987100	0.06061200	0.91981000
C	5.33656000	-1.35883500	-0.75664900
H	3.60131400	-1.72572200	-1.97364600
C	4.97560000	-0.02699600	1.22029800
H	2.95356000	0.60296200	1.58350700
C	5.83665400	-0.74002100	0.38625700
H	6.00123000	-1.91247100	-1.41285500
H	5.35886300	0.45411000	2.11526200
H	6.89292600	-0.81102100	0.62692700

A.2.0.9. $C_6H_4(PSi(SiMe_3)_2Si$ *cis*

[C6H4P(Si(SiMe3)3)2Si] cis
Energy: -4237.94509214

C	-0.77931900	-1.66996300	-0.62129600
C	0.59294600	-1.63096700	-0.28222400
C	1.26880200	-2.82374300	0.01406500
C	0.60248200	-4.03836500	-0.01284200
C	-0.75283300	-4.08295400	-0.34874300
C	-1.42947100	-2.91233100	-0.65842300
H	2.32321000	-2.79265000	0.26466000
H	1.13732000	-4.95305600	0.22256600
H	-1.27691400	-5.03299400	-0.37779000
H	-2.47531300	-2.95634600	-0.94099200
P	1.33817300	0.00795200	-0.22252600
Si	4.68037800	-0.94567100	-1.84985000
Si	3.59064700	0.17748700	-0.05778300
Si	4.24055800	-0.57583800	2.10572500
Si	3.99123500	2.52363300	-0.21137700
C	4.11175400	-2.73605200	-2.06125100
H	3.03603700	-2.80339200	-2.24392300
H	4.62893300	-3.17954000	-2.92019300
H	4.34369500	-3.34779000	-1.18422100
C	6.54413200	-0.96048200	-1.50000000
H	6.78244300	-1.53099200	-0.59658600
H	7.07458000	-1.43157400	-2.33563900
H	6.95007700	0.04748200	-1.37541300
C	4.36125300	-0.02962100	-3.47324000
H	3.29033200	0.11106700	-3.64773200
H	4.83773100	0.95520000	-3.48709800

H	4.76556200	-0.60464200	-4.31415600
C	5.88553800	0.24036400	2.57625600
H	6.22247300	-0.14076400	3.54708600
H	6.67189200	0.02683500	1.84556300
H	5.79266400	1.32690900	2.66279200
C	4.50701200	-2.45050100	2.19589300
H	5.20414000	-2.81040800	1.43288700
H	4.92987000	-2.70697300	3.17437000
H	3.57103100	-3.00606000	2.09074900
C	2.92147400	-0.09169900	3.36832600
H	2.77680600	0.99195400	3.40439800
H	1.95438900	-0.54298700	3.12758100
H	3.21255800	-0.42687600	4.37042500
C	5.86202900	2.80977400	-0.32273000
H	6.06374100	3.88719600	-0.30820400
H	6.41289200	2.35720500	0.50603600
H	6.27156600	2.41352400	-1.25707700
C	3.20888500	3.29918000	-1.74591500
H	3.54026700	2.81323900	-2.66747000
H	2.11680800	3.24933000	-1.71536300
H	3.49626300	4.35598900	-1.80164800
C	3.32112700	3.40828200	1.32091900
H	2.24771100	3.23320000	1.44111700
H	3.82126400	3.08501200	2.23900500
H	3.47353200	4.48930200	1.22283500
P	-1.58171100	-0.11959700	-1.13900300
Si	-3.57924700	0.17769300	-0.05703500
Si	-5.30359400	-0.74083600	-1.40663300
Si	-3.93380300	2.52861500	0.06527500
Si	-3.49853100	-0.73477000	2.13465100
C	-4.92778200	-2.49538600	-2.01284300
H	-4.03125500	-2.52233700	-2.63967800
H	-4.79267200	-3.19982500	-1.18637900
H	-5.76517200	-2.85782300	-2.62054600
C	-5.56529800	0.33857500	-2.94030300
H	-6.31700400	-0.11301600	-3.59784900
H	-5.91159600	1.34367500	-2.68155500
H	-4.63794200	0.44003000	-3.51275600
C	-6.91849200	-0.81068400	-0.41518100
H	-7.21280400	0.17182500	-0.03552300
H	-7.73185100	-1.17936200	-1.05077300
H	-6.83664700	-1.48883800	0.44036800
C	-3.77697900	-2.60705400	2.15095600
H	-3.79603600	-2.96761800	3.18622100
H	-4.72999900	-2.88295600	1.68827100
H	-2.97644800	-3.13590800	1.62716600
C	-4.86892100	0.04544700	3.19048300
H	-5.86370700	-0.15690400	2.78107600
H	-4.83785600	-0.37332600	4.20322800
H	-4.75655100	1.13014900	3.27880900
C	-1.81951900	-0.34947900	2.91002000
H	-1.00708100	-0.78208900	2.31844000
H	-1.64479400	0.72849700	2.97556900
H	-1.76187100	-0.76416600	3.92301600
C	-2.92566900	3.30633900	1.46543200
H	-3.19245700	2.89316500	2.44277200
H	-1.85210500	3.15758800	1.31467300
H	-3.10996700	4.38647900	1.49877900
C	-3.48872600	3.39884200	-1.55476500
H	-4.05086800	2.99986600	-2.40366500
H	-3.71804700	4.46781100	-1.47204700
H	-2.42279300	3.30537300	-1.78323300
C	-5.77012400	2.84854700	0.41737400
H	-5.93668100	3.92426700	0.54714000
H	-6.40700100	2.51549400	-0.40794300
H	-6.11143800	2.34900500	1.32890400

Si	-0.12461600	1.53060100	-0.72853900

A.2.0.10. $C_6H_4(PSi(SiMe_3)_2Si$ *trans*

[C6H4P(Si(SiMe3)3)2Si] cis
Energy: -4237.94201033

C	0.67761800	1.57768100	-0.20022700
C	-0.67764600	1.57740800	0.19951200
C	-1.33616700	2.80205800	0.38641100
C	-0.67220100	4.00362000	0.19115400
C	0.67152000	4.00389800	-0.19040100
C	1.33577200	2.80262600	-0.38647700
H	-2.37590100	2.80883000	0.69591400
H	-1.19729600	4.94167600	0.34037500
H	1.19637400	4.94217500	-0.33908400
H	2.37544000	2.80988200	-0.69617300
P	-1.42452800	-0.03104600	0.57630200
P	1.42484800	-0.03035100	-0.57837000
Si	3.61472600	-0.19405000	0.03676100
Si	4.08810600	-2.52291400	-0.14063200
Si	4.87643900	1.04061700	-1.57174500
Si	3.81142200	0.51224200	2.29567000
Si	-4.87500000	1.03846300	1.57439600
Si	-3.61487800	-0.19403800	-0.03705100
Si	-4.08803100	-2.52309000	0.13810500
Si	-3.81306100	0.51527000	-2.29493300
C	3.83879200	1.26522800	-3.13688200
H	2.92079300	1.82973000	-2.94904000
H	4.41539800	1.79995300	-3.90053500
H	3.54163300	0.29797300	-3.55347300
C	5.40517900	2.73817500	-0.91291000
H	4.56422500	3.35888400	-0.59143900
H	6.08481800	2.63507000	-0.06090100
H	5.94123300	3.28512300	-1.69727600
C	6.47307600	0.14234600	-2.05492200
H	6.27313800	-0.80950800	-2.55556700
H	7.04209300	0.76845700	-2.75204900
H	7.11427900	-0.05748100	-1.19127700
C	3.75130800	2.39266600	2.49812200
H	2.82533800	2.81021700	2.09286500
H	3.79186100	2.64225600	3.56506500
H	4.59240600	2.89154300	2.00878200
C	2.38650000	-0.22630300	3.29220400
H	1.42328000	0.14448900	2.92812100
H	2.36263800	-1.31811100	3.23632800
H	2.47919000	0.05561400	4.34747200
C	5.46315800	-0.10258500	2.99735800
H	6.31514900	0.26827100	2.41829800
H	5.58646300	0.24978400	4.02793300
H	5.51871600	-1.19538100	3.01361400
C	3.51587300	-3.17481300	-1.82162600
H	4.00442100	-2.65223400	-2.65007400
H	3.75140600	-4.24133700	-1.91347500
H	2.43482900	-3.05943700	-1.94540500
C	3.24433200	-3.51543400	1.23068400
H	3.61644300	-3.23416500	2.22083100
H	2.15821600	-3.38731800	1.22425500
H	3.45656300	-4.58187700	1.08921600
C	5.95122600	-2.82235200	0.03446700

H	6.35192100	-2.39401400	0.95806900
H	6.13760100	-3.90225100	0.06369300
H	6.52038100	-2.40988900	-0.80138600
C	-3.83512200	1.26254900	3.13811400
H	-2.91758200	1.82745400	2.94925500
H	-4.41079500	1.79665300	3.90290300
H	-3.53706900	0.29514100	3.55370500
C	-6.47015300	0.13857600	2.05946400
H	-6.26869700	-0.81425400	2.55764600
H	-7.03774400	0.76300600	2.75925800
H	-7.11336000	-0.05962100	1.19693500
C	-5.40589400	2.73622600	0.91780600
H	-4.56567000	3.35820500	0.59684500
H	-6.08571600	2.63349400	0.06589400
H	-5.94221200	3.28167100	1.70303900
C	-5.95115200	-2.82241200	-0.03714700
H	-6.13756200	-3.90229900	-0.06665200
H	-6.52040500	-2.41013900	0.79872700
H	-6.35173600	-2.39386800	-0.96070000
C	-3.51553100	-3.17634500	1.81847600
H	-4.00400200	-2.65446600	2.64740800
H	-3.75096400	-4.24295900	1.90950200
H	-2.43447900	-3.06097600	1.94219000
C	-3.24432300	-3.51437800	-1.23414600
H	-3.61605800	-3.23185600	-2.22408100
H	-2.15815700	-3.38668100	-1.22734400
H	-3.45700400	-4.58089900	-1.09393900
C	-5.46443800	-0.09993100	-2.99712600
H	-5.58830800	0.25404100	-4.02708300
H	-5.51902500	-1.19274400	-3.01519700
H	-6.31660000	0.26922300	-2.41723500
C	-3.75480000	2.39603400	-2.49478800
H	-4.59597800	2.89344700	-2.00408000
H	-2.82889700	2.81390400	-2.08971000
H	-3.79646400	2.64707900	-3.56134800
C	-2.38773800	-0.22080300	-3.29270100
H	-1.42474100	0.15005600	-2.92810000
H	-2.36317000	-1.31268600	-3.23841400
H	-2.48067700	0.06259900	-4.34754700
Si	0.00028400	-1.61256600	-0.00136000

A.3. Germylene

A.3.0.11. $C_6H_4(P^iPr)_2Ge$ *cis*

[C6H4P(iPR)2Ge] cis
Energy: -3227.61361825

C	-3.68372700	-0.38276300	0.70224600
C	-2.50642000	-0.08959700	1.39949100
C	-1.30523200	0.17334000	0.71100800
C	-1.30523200	0.17334000	-0.71100800
C	-2.50642000	-0.08959700	-1.39949100
C	-3.68372700	-0.38276300	-0.70224600
H	-4.59499800	-0.60306700	1.24847900
H	-2.52467700	-0.07216100	2.48420900
H	-2.52467700	-0.07216100	-2.48420900
H	-4.59499800	-0.60306700	-1.24847900

P	0.27281700	0.58270400	-1.57941700
P	0.27281700	0.58270400	1.57941700
Ge	2.00707800	0.09761400	0.00000000
C	0.31145500	-0.41799600	3.20914000
C	-0.21686600	0.43633300	4.37455400
C	1.73519900	-0.91600400	3.49919100
H	-0.34790600	-1.27926900	3.05050200
H	-1.22658000	0.81436600	4.18863600
H	-0.23991600	-0.15692000	5.29727200
H	0.43265100	1.30211800	4.54009000
H	2.07053300	-1.64067500	2.75071300
H	2.45097500	-0.08590300	3.51636700
H	1.76795700	-1.40074400	4.48213200
C	0.31145500	-0.41799600	-3.20914000
C	1.73519900	-0.91600400	-3.49919100
C	-0.21686600	0.43633300	-4.37455400
H	-0.34790600	-1.27926900	-3.05050200
H	2.07053300	-1.64067500	-2.75071300
H	1.76795700	-1.40074400	-4.48213200
H	2.45097500	-0.08590300	-3.51636700
H	-1.22658000	0.81436600	-4.18863600
H	0.43265100	1.30211800	-4.54009000
H	-0.23991600	-0.15692000	-5.29727200

A.3.0.12. $C_6H_4(P^iPr)_2Ge$ *trans*

[C6H4P(iPR)2Ge] trans
Energy: -3227.61051475

C	-0.69725600	3.74832400	0.08889700
C	-1.38662700	2.53620900	0.19761300
C	-0.69864900	1.30842800	0.11490100
C	0.69886700	1.30852000	-0.11628500
C	1.38658500	2.53647200	-0.19861100
C	0.69703900	3.74845600	-0.08943900
H	-1.23858400	4.68617600	0.15710200
H	-2.45801700	2.54822400	0.36921600
H	2.45794700	2.54872100	-0.37029600
H	1.23822900	4.68640900	-0.15732900
P	-1.52638200	-0.30828900	0.43742000
P	1.52725100	-0.30789700	-0.43961000
Ge	0.00018000	-2.07526100	-0.00114200
C	3.26692900	-0.25844800	0.34879000
C	4.32588600	0.15230900	-0.68933000
C	3.61248400	-1.61724500	0.97620500
H	3.20926700	0.49932800	1.13889400
H	4.10063700	1.11629900	-1.15499500
H	5.31077200	0.22752100	-0.21180900
H	4.39019000	-0.59280300	-1.48919000
H	2.93032100	-1.86717700	1.79353700
H	3.56283400	-2.42097700	0.23236700
H	4.63477800	-1.59569200	1.37253200
C	-3.26791100	-0.25815600	-0.34647800
C	-4.32416300	0.15262700	0.69438200
C	-3.61534200	-1.61665300	-0.97353900
H	-3.21200800	0.49988800	-1.13645900
H	-4.09735500	1.11636600	1.15982700
H	-5.31018500	0.22837800	0.21929900

```
 H                  -4.38678100   -0.59275000    1.49412200
 H                  -2.93512300   -1.86655400   -1.79249200
 H                  -3.56423900   -2.42062200   -0.23006200
 H                  -4.63853500   -1.59465200   -1.36751100
```

A.3.0.13. $C_6H_4(P^tBu)_2Ge$ *cis*

```
[C6H4P(tBu)2Ge] cis
Energy: -3306.2398121

 C                   0.69414000    3.71728500    0.04409800
 C                   1.38279700    2.53655300   -0.15591900
 C                   0.70864200    1.31918500   -0.30241400
 C                  -0.70866200    1.31917200   -0.30236900
 C                  -1.38284000    2.53652000   -0.15582600
 C                  -0.69420000    3.71726900    0.04414600
 H                   1.24028600    4.64245400    0.18381700
 H                   2.46376400    2.56510800   -0.19594700
 H                  -2.46381100    2.56502800   -0.19577300
 H                  -1.24036000    4.64242500    0.18390300
 P                  -1.53064300   -0.25351900   -0.67622500
 P                   1.53065700   -0.25348600   -0.67632700
 C                  -4.26669600    0.30549100   -0.38547900
 H                  -5.21335400    0.08752300    0.11939000
 H                  -4.12183700    1.38522200   -0.34206600
 H                  -4.36742400    0.02363800   -1.43473600
 C                  -3.47351500   -1.96544600    0.21601800
 H                  -3.50978400   -2.31927500   -0.81671200
 H                  -2.74828300   -2.57568100    0.75692300
 H                  -4.45717600   -2.13743600    0.66284200
 C                  -2.99683800   -0.04959200    1.75209200
 H                  -3.95162800   -0.18526900    2.27158500
 H                  -2.24286400   -0.64829700    2.26563300
 H                  -2.71207500    0.99880400    1.84585200
 C                   4.26677400    0.30562600   -0.38539800
 H                   4.12187000    1.38535100   -0.34197100
 H                   5.21341400    0.08770100    0.11952400
 H                   4.36759600    0.02380900   -1.43465600
 C                   3.47357800   -1.96551600    0.21599600
 H                   2.74834500   -2.57580800    0.75683900
 H                   3.50991000   -2.31931100   -0.81674500
 H                   4.45722200   -2.13750800    0.66285700
 C                   2.99672600   -0.04961200    1.75220500
 H                   2.24272700   -0.64834000    2.26568300
 H                   3.95148100   -0.18529800    2.27176100
 H                   2.71195100    0.99877900    1.84599800
 Ge                  0.00001200   -1.89748800   -0.24665900
 C                  -3.13796100   -0.47588900    0.29368900
 C                   3.13795900   -0.47587100    0.29372200
```

A.3.0.14. $C_6H_4(P^tBu)_2Ge$ *trans*

```
[C6H4P(tBu)2Ge] trans
```

Energy: -3306.23590096

C	-0.68082900	3.72608300	0.14077900
C	-1.35336000	2.52878400	0.29367400
C	-0.68709600	1.30741400	0.15373600
C	0.68734700	1.30747700	-0.15490900
C	1.35345900	2.52895000	-0.29458800
C	0.68086000	3.72616700	-0.14130400
H	-1.21495900	4.66197500	0.25235600
H	-2.40567300	2.54625500	0.54311300
H	2.40573200	2.54656700	-0.54419300
H	1.21492100	4.66212600	-0.25264500
P	-1.42755400	-0.30345200	0.51806300
C	-4.15174900	0.26384900	0.91131300
H	-3.98707500	1.33970100	0.96753100
H	-5.18865800	0.10929200	0.59668500
H	-4.03765100	-0.14532100	1.91649600
C	-3.54899800	-1.91922100	-0.10232800
H	-2.95863400	-2.45608700	-0.84599200
H	-3.37832700	-2.38789000	0.86977200
H	-4.60682800	-2.04498200	-0.35117400
C	-3.37649900	0.16066300	-1.47972100
H	-2.73915100	-0.35411900	-2.20014400
H	-4.41686900	0.05166100	-1.80377400
H	-3.12684200	1.22188100	-1.50985300
P	1.42826500	-0.30313300	-0.51993500
C	3.37338700	0.15981100	1.48191400
H	3.12364700	1.22101300	1.51213000
H	2.73459800	-0.35539200	2.20075900
H	4.41311500	0.05064300	1.80797600
C	3.54875800	-1.91925000	0.10350500
H	3.37979700	-2.38732100	-0.86918500
H	4.60617700	-2.04508800	0.35406200
H	2.95720200	-2.45667500	0.84581900
C	4.15321100	0.26454300	-0.90743400
H	5.18953300	0.10949500	-0.59111900
H	4.04079300	-0.14367700	-1.91319300
H	3.98884500	1.34047800	-0.96288900
Ge	0.00021500	-1.98976000	-0.00098800
C	-3.21119300	-0.42708600	-0.08076100
C	3.21082800	-0.42708700	0.08231600

A.3.0.15. $C_6H_4(PSiMe_3)_2Ge$ *cis*

[C6H4(P(SiMe3))2Ge] cis
Energy: -3808.82681073

C	0.70102600	3.72360500	0.02856200
C	1.39078600	2.54870800	-0.28840700
C	0.71391600	1.34392300	-0.58347400
C	-0.71391500	1.34392700	-0.58347600
C	-1.39077900	2.54871600	-0.28840800
C	-0.70101300	3.72360900	0.02856300
H	1.25534800	4.63326600	0.25695100
H	2.48022200	2.56899600	-0.31617500
H	-2.48021500	2.56901000	-0.31617500
H	-1.25533000	4.63327200	0.25695300
P	-1.72775800	-0.11102600	-1.13925100
P	1.72775800	-0.11103000	-1.13925100
Si	-3.20796000	-0.54457200	0.57429000
C	-4.72590900	0.55601800	0.26237800
H	-5.53427200	0.27174500	0.95448000

```
 H                  -4.51603500    1.62220800    0.42768300
 H                  -5.10669500    0.43993600   -0.76215900
 C                  -3.69513000   -2.36002000    0.33611300
 H                  -3.97563800   -2.56188400   -0.70766200
 H                  -2.88125400   -3.04387500    0.60838700
 H                  -4.56406300   -2.60180100    0.96762900
 C                  -2.48807200   -0.18349100    2.28780900
 H                  -3.28048500   -0.24236300    3.05060200
 H                  -1.70174800   -0.90072800    2.55529600
 H                  -2.05740100    0.82706600    2.32948300
 Si                  3.20795700   -0.54458000    0.57429100
 C                   4.72582500    0.55615200    0.26248100
 H                   4.51585600    1.62231500    0.42783700
 H                   5.53419000    0.27190700    0.95459200
 H                   5.10665300    0.44015800   -0.76205100
 C                   3.69528400   -2.35997400    0.33601400
 H                   2.88146400   -3.04391300    0.60823200
 H                   3.97583100   -2.56175300   -0.70776700
 H                   4.56422800   -2.60171800    0.96753100
 C                   2.48800000   -0.18365800    2.28781200
 H                   1.70171600   -0.90096800    2.55523000
 H                   3.28039500   -0.24252700    3.05062400
 H                   2.05725500    0.82686600    2.32954100
 Ge                 -0.00000300   -1.59347900   -0.78585800
```

A.3.0.16. $C_6H_4(PSiMe_3)_2Ge$ *trans*

```
[C6H4(P(SiMe3))2Ge] trans
Energy: -3808.82137055
 C                  -0.57504200    3.62938900    0.32394800
 C                  -1.04380300    2.37800500    0.74118700
 C                  -0.45357500    1.17505700    0.29108600
 C                   0.66682500    1.25107900   -0.59047300
 C                   1.09908300    2.52428900   -1.02506600
 C                   0.49657200    3.70485300   -0.57590900
 H                  -1.05253200    4.53619000    0.69413200
 H                  -1.87641000    2.33347000    1.44322000
 H                   1.92951100    2.58669500   -1.72925700
 H                   0.86064600    4.66967600   -0.92695300
 P                  -1.17146900   -0.42071600    0.93025200
 Si                 -3.32034400   -0.44116000    0.08553600
 C                  -4.37861300    0.54461200    1.31877800
 H                  -4.15741900    1.62081100    1.29510800
 H                  -5.44306600    0.42518000    1.06177900
 H                  -4.24203200    0.19008600    2.35020100
 C                  -3.85089800   -2.25968000    0.12647100
 H                  -3.33221400   -2.85698100   -0.63417300
 H                  -3.64875400   -2.70868900    1.10967800
 H                  -4.93288600   -2.33998400   -0.06094600
 C                  -3.44815300    0.34108300   -1.63297500
 H                  -3.01637800   -0.30683700   -2.40561300
 H                  -4.50379300    0.52493100   -1.88732600
 H                  -2.92185500    1.30546600   -1.66247500
 P                   1.65089900   -0.18782600   -1.25411100
 Si                  3.18949700   -0.48113600    0.44925600
 C                   2.44071700   -0.74309100    2.16904100
 H                   1.66369700    0.00234800    2.38757500
 H                   1.99458100   -1.73957900    2.27838700
 H                   3.22910100   -0.63828000    2.93162400
 C                   4.26677800   -1.94850800   -0.07801200
 H                   4.72243500   -1.77849200   -1.06390400
```

H	5.08256900	-2.09364400	0.64741000
H	3.69115700	-2.88270200	-0.12317600
C	4.21093900	1.11896200	0.44072600
H	5.02379800	1.04216800	1.17986000
H	4.66867500	1.30655500	-0.54109900
H	3.60126500	1.99407300	0.70542400
Ge	0.02235400	-1.67026500	-0.58535900

A.3.0.17. $C_6H_4(Ph)_2Ge$ *cis*

[C6H4P(Ph)2Ge] cis
Energy: -1380.57299296

C	0.69838200	3.72565200	-0.01386000
C	1.39641000	2.55871800	-0.34212900
C	0.70437600	1.36813400	-0.64365900
C	-0.71326600	1.36950000	-0.64843600
C	-1.40502100	2.56141700	-0.35156800
C	-0.70697300	3.72700600	-0.01859500
H	1.24429700	4.62973800	0.23453600
H	2.48150300	2.56629600	-0.35708500
H	-2.48997200	2.57108700	-0.37383600
H	-1.25280600	4.63214500	0.22612200
P	-1.61415300	-0.15963200	-1.18517100
P	1.60591100	-0.16273400	-1.17432100
Ge	-0.00695200	-1.93348100	-0.84630900
C	3.04283000	-0.36602700	-0.00576900
C	3.60076800	0.79311100	0.56585500
C	3.59821600	-1.62093500	0.30921900
C	4.70328000	0.70068500	1.42840000
H	3.16788700	1.76356700	0.34419800
C	4.69011400	-1.71231100	1.18314000
H	3.17736600	-2.52178800	-0.12513000
C	5.24957800	-0.55215800	1.74171000
H	5.12460600	1.60240700	1.86049000
H	5.10818000	-2.68550000	1.41948400
H	6.09803700	-0.62494000	2.41397100
C	-3.03527900	-0.38315600	-0.00110300
C	-3.73918400	0.76353600	0.41273900
C	-3.43963200	-1.64473800	0.47573400
C	-4.83671000	0.65012100	1.27912800
H	-3.42349500	1.74242900	0.06573100
C	-4.52694400	-1.75433700	1.35327000
H	-2.90541200	-2.53619000	0.16391300
C	-5.23226700	-0.60853600	1.75403600
H	-5.37147100	1.54207500	1.58859400
H	-4.82784500	-2.73219000	1.71520600
H	-6.07683200	-0.69633800	2.42940000

A.3.0.18. $C_6H_4(Ph)_2Ge$ *trans*

[C6H4P(Ph)2Ge] trans
Energy: -1380.57254768

C	0.65777700	-3.73543800	0.24812500

C	1.30782000	-2.52431100	0.50712100
C	0.65596000	-1.29925200	0.26125500
C	-0.65596100	-1.29925300	-0.26126100
C	-1.30781900	-2.52431300	-0.50712500
C	-0.65777500	-3.73543900	-0.24812800
H	1.16722100	-4.67347900	0.44201200
H	2.31432100	-2.52700700	0.91291700
H	-2.31432000	-2.52701100	-0.91292200
H	-1.16721800	-4.67348100	-0.44201400
P	1.40008500	0.31170500	0.77693200
P	-1.40008800	0.31170200	-0.77694200
Ge	-0.00000200	2.08983800	-0.00000600
C	-3.18324900	0.30580500	-0.26665400
C	-4.10806900	1.01967200	-1.05213500
C	-3.63418000	-0.36616200	0.88593700
C	-5.46056700	1.07169000	-0.68474200
H	-3.77308200	1.52542300	-1.95232600
C	-4.98906300	-0.32514900	1.24171300
H	-2.93024700	-0.91407500	1.50340800
C	-5.90569700	0.39714400	0.46130500
H	-6.16275500	1.62805000	-1.29683600
H	-5.32540300	-0.84756000	2.13138400
H	-6.95297600	0.43168100	0.74255600
C	3.18324900	0.30580700	0.26665600
C	4.10806400	1.01967300	1.05214300
C	3.63418600	-0.36616000	-0.88593300
C	5.46056500	1.07169000	0.68475800
H	3.77307300	1.52542300	1.95233200
C	4.98907100	-0.32514800	-1.24170100
H	2.93025700	-0.91407100	-1.50340900
C	5.90570100	0.39714500	-0.46128600
H	6.16275000	1.62804900	1.29685700
H	5.32541600	-0.84755800	-2.13137100
H	6.95298200	0.43168100	-0.74253200

A.3.0.19. $C_6H_4(PSi(SiMe_3)_2Ge$ *cis*

[C6H4P(Si(SiMe3)3)2Ge] cis
Energy: -6023.33336

C	0.79117900	1.76817700	-0.71118200
C	-0.79118300	1.76817100	-0.71118000
C	-1.44859700	2.91014800	-0.43354000
C	-0.70949600	4.07779100	-0.15046900
C	0.70947400	4.07779400	-0.15046200
C	1.44858400	2.91015500	-0.43352900
H	-2.51836800	2.93156900	-0.42772800
H	-1.23152700	4.98549900	0.06963800
H	1.23149900	4.98550000	0.06964700
H	2.51835500	2.93158000	-0.42770800
P	-1.62329300	0.16502100	-1.09705600
Si	-5.13491300	1.39087700	-0.91673000
Si	-3.59432400	-0.18940400	-0.13900400
Si	-3.37991200	0.00733100	2.18282700
Si	-4.34580100	-2.34008800	-0.67329900
C	-4.51189800	3.17389500	-0.47365100
H	-3.56186400	3.34474000	-0.93533000
H	-5.21637100	3.89648900	-0.82928600
H	-4.41384300	3.26387200	0.58804000
C	-6.85738300	1.08113000	-0.07964200
H	-6.75930700	1.17110600	0.98204900

H	-7.56185800	1.80372600	-0.43526300
H	-7.20100400	0.09771400	-0.32401500
C	-5.31270600	1.22776100	-2.84167100
H	-4.36267300	1.39860200	-3.30335600
H	-5.65633300	0.24435200	-3.08605700
H	-6.01717400	1.95036800	-3.19729100
C	-5.10245400	-0.30240900	3.01979500
H	-5.00445100	-0.21248400	4.08149400
H	-5.80688400	0.42022500	2.66415500
H	-5.44609100	-1.28580500	2.77535200
C	-2.75689000	1.79030600	2.62603100
H	-3.46133300	2.51293700	2.27041200
H	-2.65887700	1.88022000	3.68773400
H	-1.80683500	1.96115700	2.16440200
C	-2.10269000	-1.30284000	2.82759600
H	-2.44631400	-2.28623800	2.58315800
H	-1.15264100	-1.13198500	2.36595300
H	-2.00466800	-1.21291500	3.88929300
C	-6.06827600	-2.64980700	0.16382200
H	-6.41188200	-3.63324600	-0.08048000
H	-5.97020700	-2.55975300	1.22550900
H	-6.77276500	-1.92724700	-0.19184900
C	-4.52364600	-2.50338200	-2.59822300
H	-5.22814500	-1.78082800	-2.95389200
H	-3.57363300	-2.33256200	-3.05995000
H	-4.86725900	-3.48682600	-2.84250800
C	-3.06849800	-3.65013900	-0.02842200
H	-2.11847500	-3.47931100	-0.49012800
H	-2.97042800	-3.56007700	1.03326400
H	-3.41209700	-4.63358000	-0.27271700
P	1.62328900	0.16503100	-1.09705800
Si	3.59432300	-0.18940200	-0.13901000
Si	5.13489500	1.39094200	-0.91665000
Si	4.34584300	-2.34004900	-0.67339200
Si	3.37989600	0.00722700	2.18283200
C	4.51184600	3.17392700	-0.47348900
H	3.56181100	3.34477700	-0.93516400
H	4.41378200	3.26385500	0.58820700
H	5.21630800	3.89654900	-0.82908500
C	5.31270200	1.22791800	-2.84159400
H	6.01715900	1.95055300	-3.19717500
H	5.65634700	0.24452500	-3.08602500
H	4.36266800	1.39876300	-3.30327700
C	6.85736400	1.08118400	-0.07956200
H	7.20100200	0.09778500	-0.32397800
H	7.56182800	1.80380800	-0.43514500
H	6.75928000	1.17110800	0.98213300
C	2.75683600	1.79016900	2.62611700
H	2.65881400	1.88003400	3.68782500
H	3.46126800	2.51282800	2.27053800
H	1.80678200	1.96102200	2.16449000
C	5.10243600	-0.30252200	3.01980100
H	5.80685500	0.42014000	2.66419900
H	5.00442600	-0.21264800	4.08150500
H	5.44609200	-1.28590100	2.77531800
C	2.10269200	-1.30299800	2.82753400
H	1.15264400	-1.13213900	2.36589400
H	2.44633500	-2.28637900	2.58305400
H	2.00465900	-1.21312600	3.88923600
C	3.06855600	-3.65015100	-0.02858400
H	2.97047500	-3.56014100	1.03310700
H	2.11853400	-3.47931700	-0.49028800
H	3.41217400	-4.63357400	-0.27292200
C	4.52370600	-2.50325100	-2.59831900
H	5.22819500	-1.78066800	-2.95395000
H	4.86733600	-3.48667600	-2.84264700

H	3.57369300	-2.33242400	-3.06004500
C	6.06831500	-2.64977700	0.16373100
H	6.41194000	-3.63319900	-0.08061400
H	6.77279400	-1.92718900	-0.19190200
H	5.97023700	-2.55977400	1.22542200
Ge	0.00000500	-1.16880400	-0.36065700

A.3.0.20. $C_6H_4(PSi(SiMe_3)_2Ge$ *trans*

[C6H4P(Si(SiMe3)3)2Ge] trans
Energy: -6023.3332852925

C	-0.51453900	-2.17761500	-0.48463400
C	0.51425200	-2.17746200	0.48320300
C	0.99347800	-3.40440600	0.96601000
C	0.49871600	-4.61067000	0.48551000
C	-0.49812500	-4.61081800	-0.48715500
C	-0.99334800	-3.40469200	-0.96752300
H	1.76078700	-3.41214900	1.73373600
H	0.88920500	-5.54762600	0.87009100
H	-0.88827300	-5.54788500	-0.87181000
H	-1.76069700	-3.41263300	-1.73520700
P	1.11728800	-0.61521000	1.24192400
P	-1.11817900	-0.61557700	-1.24334500
Si	-2.90679800	0.18241700	-0.00025200
Si	-3.42793300	2.27904400	-1.01326500
Si	-4.65803500	-1.35944300	-0.48169500
Si	-2.71781300	0.40064000	2.36797200
Si	4.65833500	-1.35854600	0.48462000
Si	2.90697800	0.18218300	0.00021200
Si	3.42698500	2.27974000	1.01191400
Si	2.71929300	0.39909700	-2.36809900
Ge	-0.00084400	0.98783000	-0.00066000
C	-4.56602400	-1.86633400	-2.30304200
H	-3.56308700	-2.18941500	-2.59425900
H	-5.26308500	-2.68876900	-2.50118100
H	-4.83793500	-1.03301300	-2.95756900
C	-4.51198900	-2.90242600	0.60551600
H	-3.52510200	-3.36748300	0.52698900
H	-4.69044700	-2.66952100	1.65996000
H	-5.25975600	-3.64404500	0.30068700
C	-6.36969500	-0.59670700	-0.19358400
H	-6.56458600	0.23010500	-0.88348000
H	-7.13932100	-1.35777800	-0.36874800
H	-6.49884500	-0.22321600	0.82606400
C	-2.03581600	-1.14368600	3.21917400
H	-0.95625400	-1.24235800	3.07729000
H	-2.22373900	-1.07143900	4.29695900
H	-2.50844600	-2.05921700	2.85370000
C	-1.70369200	1.90230800	2.92872900
H	-0.66570200	1.84854000	2.58870100
H	-2.13237800	2.83807600	2.55583700
H	-1.70031700	1.94957300	4.02421900
C	-4.48445900	0.65459300	3.01572600
H	-5.09370800	-0.24440100	2.88098900
H	-4.44877500	0.86918700	4.09028600
H	-4.99817200	1.48681900	2.52658300
C	-3.86260300	2.00422000	-2.83516600
H	-4.78310200	1.42413200	-2.95129100
H	-4.01164900	2.96735100	-3.33667600

H	-3.06307200	1.47192800	-3.35938600
C	-2.04415300	3.57006800	-0.93686800
H	-1.68725600	3.73518000	0.08371100
H	-1.17124300	3.28768600	-1.53069500
H	-2.43344400	4.51972000	-1.32459600
C	-4.92149300	3.04543400	-0.13010500
H	-4.67040100	3.33945100	0.89399600
H	-5.23598400	3.95089500	-0.66212300
H	-5.78004400	2.37016400	-0.08473300
C	4.56424000	-1.86420300	2.30620500
H	3.56104800	-2.18754600	2.59626200
H	5.26142000	-2.68616300	2.50588900
H	4.83482000	-1.03028300	2.96051900
C	6.37002900	-0.59537600	0.19782500
H	6.56404300	0.23176700	0.88757100
H	7.13974400	-1.35613400	0.37393400
H	6.49995000	-0.22221800	-0.82185500
C	4.51426400	-2.90241200	-0.60164800
H	3.52741300	-3.36772500	-0.52415600
H	4.69410800	-2.67024100	-1.65602100
H	5.26184000	-3.64358100	-0.29526300
C	4.92106100	3.04553200	0.12908100
H	5.23498600	3.95155600	0.66047600
H	5.77976400	2.37036900	0.08500400
H	4.67070500	3.33853800	-0.89549000
C	3.86065100	2.00645400	2.83428500
H	4.78089300	1.42614000	2.95133800
H	4.00980400	2.96996100	3.33503800
H	3.06069500	1.47489000	3.35860100
C	2.04328300	3.57075000	0.93359000
H	1.68704100	3.73507500	-0.08734700
H	1.16997500	3.28899800	1.52713400
H	2.43243400	4.52069100	1.32075000
C	4.48619900	0.65233600	-3.01537600
H	4.45108500	0.86550800	-4.09023400
H	4.99957300	1.48524900	-2.52704100
H	5.09545100	-0.24641700	-2.87908300
C	2.03719200	-1.14547400	-3.21878100
H	2.51015000	-2.06086300	-2.85335900
H	0.95771200	-1.24436500	-3.07645200
H	2.22463700	-1.07337600	-4.29666000
C	1.70552000	1.90066800	-2.92974400
H	0.66758900	1.84742500	-2.58943800
H	2.13454300	2.83654700	-2.55752000
H	1.70189100	1.94724100	-4.02525500

A.4. Stannylene

A.4.0.21. $C_6H_4(P^iPr)_2Sn$ *cis*

[C6H4P(iPr)2Sn] cis
Energy: -7175.7241421

C	1.50065500	-0.11273600	0.70774800
C	1.50065500	-0.11273600	-0.70774800
C	2.69837000	0.14056900	-1.38333200

C	3.86346100	0.42416000	−0.69481400
C	3.86346100	0.42416000	0.69481400
C	2.69837000	0.14056900	1.38333200
H	2.71759600	0.13123700	−2.46611500
H	4.77285000	0.64254200	−1.24163100
H	4.77285000	0.64254200	1.24163100
H	2.71759600	0.13123700	2.46611500
P	−0.03720400	−0.52184900	−1.56642300
P	−0.03720400	−0.52184900	1.56642300
Sn	−1.90167900	0.02238400	0.00000000
C	−0.01140400	0.30159000	3.24583500
C	0.55365200	−0.64388800	4.30452900
C	−1.40704700	0.77427500	3.63582200
H	0.64314000	1.17169600	3.14785300
H	1.54873100	−1.00909200	4.04779300
H	0.61949900	−0.13574000	5.27111900
H	−0.09180100	−1.51681500	4.42394000
H	−1.76695100	1.56457100	2.97547400
H	−2.12911400	−0.04607900	3.60411500
H	−1.40003600	1.16199500	4.65800700
C	−0.01140400	0.30159000	−3.24583500
C	−1.40704700	0.77427500	−3.63582200
C	0.55365200	−0.64388800	−4.30452900
H	0.64314000	1.17169600	−3.14785300
H	−1.76695100	1.56457100	−2.97547400
H	−1.40003600	1.16199500	−4.65800700
H	−2.12911400	−0.04607900	−3.60411500
H	1.54873100	−1.00909200	−4.04779300
H	−0.09180100	−1.51681500	−4.42394000
H	0.61949900	−0.13574000	−5.27111900

A.4.0.22. $C_6H_4(P^iPr)_2Sn$ *trans*

[C6H4P(iPr)2Sn] trans
Energy: −7175.72047076

C	−0.37251200	1.71361300	−0.38169200
C	0.93046600	1.27809700	0.09909700
C	1.96791400	2.21172200	0.21057700
C	1.74820700	3.55351800	−0.13429900
C	0.49146300	3.97349100	−0.59842500
C	−0.56358700	3.05770400	−0.72411700
H	2.93048100	1.90098700	0.55958900
H	2.54458900	4.26232000	−0.04332200
H	0.33741100	4.99988600	−0.85858100
H	−1.51650000	3.38703700	−1.08244000
P	1.23964100	−0.49149800	0.53814600
P	−1.76628300	0.51320000	−0.57006700
Sn	−0.57938600	−1.58444400	−0.60530300
C	−2.92901800	0.59346800	0.82779000
C	−2.16623600	0.35557100	2.14428800
C	−4.01085700	−0.48937500	0.65845300
H	−3.39092200	1.55831600	0.85255300
H	−1.41456800	1.10793600	2.26194400
H	−2.84982200	0.40276100	2.96610500
H	−1.70433200	−0.60927700	2.11952500
H	−4.54084200	−0.32408300	−0.25625600
H	−3.54895300	−1.45422300	0.63369100
H	−4.69444300	−0.44218500	1.48027000
C	2.88060100	−1.07261100	0.00715000
C	3.03001300	−2.56754500	0.34545300
C	3.97141600	−0.26909000	0.73932300

```
 H                 2.98362600   -0.93385700   -1.04880200
 H                 2.27210900   -3.12583500   -0.16326500
 H                 3.99475400   -2.90918800    0.03327400
 H                 2.92698800   -2.70629900    1.40140400
 H                 3.86760400    0.76959800    0.50426800
 H                 3.86839100   -0.40784400    1.79527400
 H                 4.93615600   -0.61073300    0.42714400
```

A.4.0.23. $C_6H_4(P^tBu)_2Sn$ *cis*

```
[C6H4P(tBu)2Sn] cis
Energy:-7254.3471742

 C                 0.70958300    1.48893300   -0.28099200
 C                -0.70930500    1.48945300   -0.28374400
 C                -1.37833600    2.71197200   -0.14878800
 C                -0.69377600    3.89729600    0.03528000
 C                 0.69541500    3.89665900    0.03766700
 C                 1.37956500    2.71072600   -0.14376200
 H                -2.45875900    2.73706500   -0.18426400
 H                -1.24250200    4.82260800    0.16318400
 H                 1.24454400    4.82147800    0.16740200
 H                 2.46013600    2.73483400   -0.17497800
 P                -1.57963200   -0.06404000   -0.62476500
 P                 1.57737300   -0.06663100   -0.61587200
 Sn               -0.00193500   -1.91736300   -0.09730800
 C                -3.20545800    0.36028800    1.67878000
 C                -4.30891200    0.60230000   -0.57095300
 C                -3.64202600   -1.63821900    0.24661500
 H                -2.90366800    1.40650400    1.73024100
 H                -2.50183600   -0.21866100    2.27910500
 H                -4.19642600    0.27499800    2.13770700
 H                -4.11445100    1.67349600   -0.61734200
 H                -5.29351700    0.46780600   -0.11173000
 H                -4.66740000   -1.74512600    0.61248300
 H                -4.35714800    0.22925100   -1.59519500
 H                -3.60023800   -2.07037300   -0.75603800
 H                -2.99269900   -2.22642600    0.89799500
 C                 3.21564600    0.36095700    1.67658900
 H                 4.20925500    0.27705900    2.12999300
 H                 2.91326600    1.40695800    1.72846900
 H                 2.51587400   -0.21785600    2.28148600
 C                 4.30706600    0.59935700   -0.57990600
 H                 4.11199900    1.67036800   -0.62798100
 H                 5.29403600    0.46617300   -0.12542300
 H                 4.35015500    0.22382200   -1.60346700
 C                 3.64377700   -1.63974800    0.24526000
 H                 2.99642500   -2.22663100    0.89976700
 H                 3.59807400   -2.07309600   -0.75668100
 H                 4.67042000   -1.74661500    0.60753600
 C                -3.25699900   -0.15758600    0.24425700
 C                 3.25960700   -0.15895300    0.24247800
```

A.4.0.24. $C_6H_4(P^tBu)_2Sn$ *trans*

```
[C6H4P(tBu)2Sn] trans
```

Energy: -7254.34460278

C	-0.71250900	1.53172300	-0.42932300
C	0.64072900	1.49177200	-0.03672300
C	1.34002700	2.69116800	0.13109100
C	0.72636000	3.91141200	-0.09005600
C	-0.59442300	3.95679300	-0.51065400
C	-1.29307000	2.77432500	-0.69375800
H	2.37689800	2.68268300	0.43607200
H	1.28943400	4.82656800	0.04926200
H	-1.07317100	4.90624500	-0.71747500
H	-2.29801500	2.81827000	-1.09739200
P	1.35069400	-0.14562400	0.24489700
P	-1.68931000	0.02092800	-0.80514800
Sn	-0.11992500	-1.95601100	-0.39727600
C	3.84700500	0.46803700	-0.92053400
C	3.73868300	0.44325000	1.60320700
C	3.59371500	-1.67563000	0.32344200
H	3.59705600	1.52566800	-1.00224900
H	3.51524400	-0.02368900	-1.83622200
H	4.93786100	0.38735900	-0.86726700
H	3.49512500	1.50235900	1.67848500
H	4.82817300	0.34847100	1.64762300
H	4.67907300	-1.77446300	0.41647600
H	3.31895400	-0.05583300	2.47794300
H	3.13644200	-2.19631000	1.16783400
H	3.28619000	-2.18024500	-0.59430400
C	-2.43825200	-0.22635400	1.96236700
H	-3.24479400	-0.23613100	2.70481900
H	-1.85943300	-1.14408700	2.08701700
H	-1.78275900	0.61465900	2.19509900
C	-3.81950300	-1.37783300	0.21974500
H	-3.19910000	-2.27706300	0.25964200
H	-4.63026500	-1.50664500	0.94349900
H	-4.26352200	-1.31844800	-0.77604700
C	-3.96284900	1.08685100	0.50563700
H	-3.45668700	2.00521600	0.80535100
H	-4.38287400	1.23394400	-0.49073300
H	-4.79426500	0.92738700	1.19953100
C	-3.02392900	-0.11614100	0.55707800
C	3.22466500	-0.19185700	0.30858300

A.4.1. $C_6H_4(PSiMe_3)_2Sn$ *cis*

[C6H4(P(SiMe3))2Sn] cis
Energy: -7757.23067097

C	0.70446300	1.56367700	-0.64218200
C	-0.70554100	1.56373100	-0.64310000
C	-1.38025600	2.78260900	-0.50771300
C	-0.69517800	3.96946000	-0.32667000
C	0.69398300	3.96935600	-0.32559900
C	1.37917400	2.78243000	-0.50567200
H	-2.46223800	2.79689800	-0.55578300
H	-1.24299400	4.89639400	-0.20617000
H	1.24174900	4.89620800	-0.20424000
H	2.46122600	2.79659800	-0.55214800
P	-1.65655100	0.03831200	-0.96860100
Si	-3.13976500	-0.24122000	0.71845600
P	1.65510500	0.03801900	-0.96682700
Si	3.14129000	-0.24099300	0.71751300

Sn	-0.00070600	-1.81420200	-0.71215900
C	-2.34333700	-0.08475100	2.41199300
C	-4.52698800	1.01970300	0.57635000
C	-3.85046900	-1.96094800	0.46143400
H	-1.80475800	0.86067600	2.50432800
H	-1.63250600	-0.89336300	2.59469000
H	-3.10168700	-0.11723700	3.19985900
H	-4.18770800	2.03052500	0.80981500
H	-5.32296000	0.77105600	1.28475100
H	-4.63796900	-2.15070700	1.19629000
H	-4.95873000	1.02733300	-0.42624700
H	-4.29110400	-2.06256000	-0.53253400
H	-3.09496600	-2.74108200	0.57459400
C	2.34744200	-0.08306900	2.41206400
H	3.10670600	-0.11658300	3.19900100
H	1.81029500	0.86311300	2.50500100
H	1.63563500	-0.89062900	2.59561300
C	4.52912100	1.01892200	0.57225000
H	4.19113100	2.03019500	0.80561900
H	5.32611800	0.77010800	1.27944300
H	4.95916000	1.02561000	-0.43109000
C	3.85055100	-1.96125300	0.46024900
H	3.09477900	-2.74086900	0.57512700
H	4.28947600	-2.06370000	-0.53439200
H	4.63918600	-2.15105500	1.19387500

A.4.2. $C_6H_4(PSiMe_3)_2Sn$ *trans*

[C6H4(P(SiMe3))2Sn] trans
Energy: -7757.21643175

C	-0.62568400	1.50797100	-0.32158800
C	0.62578200	1.50792100	0.32144600
C	1.21948100	2.73342600	0.64719500
C	0.61357700	3.93342200	0.32614300
C	-0.61340900	3.93346700	-0.32618700
C	-1.21935300	2.73350600	-0.64729000
H	2.16241800	2.74029000	1.18062600
H	1.09427500	4.86827800	0.58845200
H	-1.09406500	4.86836000	-0.58844300
H	-2.16229200	2.74039900	-1.18072100
P	1.42120300	-0.04322100	0.86563900
Si	3.45555200	-0.16743700	-0.11694700
P	-1.42126500	-0.04306700	-0.86582800
Si	-3.45540100	-0.16727500	0.11714600
Sn	-0.00012400	-1.90125600	-0.00009600
C	3.34922400	0.09861800	-1.97111000
C	4.61034300	1.11552300	0.62774900
C	4.09817500	-1.88436200	0.29069600
H	2.85553700	1.04511600	-2.20083600
H	2.78033700	-0.69892600	-2.45298000
H	4.34784800	0.12295800	-2.41719700
H	4.31435200	2.13229700	0.36285200
H	5.62587800	0.96185700	0.25067900
H	5.11460700	-2.00279800	-0.09528600
H	4.64079600	1.04128400	1.71657600
H	4.13085400	-2.04962800	1.36963100
H	3.48042700	-2.66848300	-0.15135000
C	-3.34882000	0.09945100	1.97119200
H	-4.34731700	0.12339200	2.41756500

H	-2.77939800	-0.69771600	2.45307000
H	-2.85548100	1.04621300	2.20056600
C	-4.09805000	-1.88438200	-0.28973200
H	-3.48085500	-2.66840100	0.15325600
H	-5.11477700	-2.00218400	0.09567700
H	-4.13012000	-2.05039100	-1.36857100
C	-4.61058800	1.11505100	-0.62805700
H	-4.31470000	2.13211400	-0.36416400
H	-4.64143300	1.03985900	-1.71681000
H	-5.62596000	0.96151800	-0.25048200

A.4.2.1. $C_6H_4(Ph)_2Sn$ *cis*

[C6H4P(Ph)2Sn] cis
Energy: -7401.9381944

C	1.47760600	-0.73403100	0.70485600
C	1.47760600	-0.73403100	-0.70485600
C	2.69590400	-0.62741400	-1.38370800
C	3.88493300	-0.47818500	-0.69531700
C	3.88493300	-0.47818500	0.69531700
C	2.69590400	-0.62741400	1.38370800
H	2.70395700	-0.64886100	-2.46716100
H	4.81434800	-0.37201600	-1.24180900
H	4.81434800	-0.37201600	1.24180900
H	2.70395700	-0.64886100	2.46716100
P	-0.06857100	-1.05652700	-1.61155800
P	-0.06857100	-1.05652700	1.61155800
Sn	-1.89107800	-0.40880500	0.00000000
C	-0.09633400	0.06895400	3.05385800
C	-0.76982400	-0.35831100	4.19907800
C	0.49495500	1.33402400	3.05766900
C	-0.86385100	0.46284300	5.31331200
H	-1.21639900	-1.34610600	4.21814400
C	0.41583100	2.14428900	4.17855300
H	1.02315500	1.68194100	2.17841000
C	-0.26844900	1.71487600	5.30829500
H	-1.39328500	0.11530100	6.19251400
H	0.88250100	3.12234400	4.16591400
H	-0.33337300	2.35316000	6.18114800
C	-0.09633400	0.06895400	-3.05385800
C	-0.76982400	-0.35831100	-4.19907800
C	0.49495500	1.33402400	-3.05766900
C	-0.86385100	0.46284300	-5.31331200
H	-1.21639900	-1.34610600	-4.21814400
C	0.41583100	2.14428900	-4.17855300
H	1.02315500	1.68194100	-2.17841000
C	-0.26844900	1.71487600	-5.30829500
H	-1.39328500	0.11530100	-6.19251400
H	0.88250100	3.12234400	-4.16591400
H	-0.33337300	2.35316000	-6.18114800

A.4.2.2. $C_6H_4(Ph)_2Sn$ *trans*

[C6H4P(Ph)2Sn] cis
Energy: -7401.9394578

C	-0.66962400	1.47970600	-0.21233500
C	0.66962000	1.47971600	0.21244200
C	1.32741300	2.69895700	0.40520200
C	0.66788700	3.89462100	0.19630300
C	-0.66792500	3.89460900	-0.19623400
C	-1.32743600	2.69893400	-0.40511200
H	2.35897600	2.70358000	0.73689000
H	1.18952400	4.83127300	0.35203000
H	-1.18957400	4.83125100	-0.35197500
H	-2.35900000	2.70353800	-0.73679600
P	1.42211300	-0.09278800	0.69604300
P	-1.42207600	-0.09282500	-0.69589300
Sn	0.00003000	-2.01364800	0.00005800
C	3.18275100	-0.06273300	0.23600700
C	4.09521000	-0.70723800	1.07260900
C	3.65261000	0.54591800	-0.93017900
C	5.44203100	-0.75576800	0.74500800
H	3.74620600	-1.16764700	1.98994200
C	5.00107800	0.51153400	-1.24430700
H	2.95741300	1.04443600	-1.59449800
C	5.89954500	-0.14333500	-0.41164500
H	6.13661700	-1.26382200	1.40332300
H	5.35138400	0.98951600	-2.15159600
H	6.95258700	-0.17328200	-0.66409800
C	-3.18275600	-0.06276500	-0.23603800
C	-4.09513800	-0.70725800	-1.07273400
C	-3.65272500	0.54587500	0.93011000
C	-5.44199000	-0.75578500	-0.74526400
H	-3.74604600	-1.16766000	-1.99003800
C	-5.00122400	0.51149400	1.24410700
H	-2.95759100	1.04438200	1.59450300
C	-5.89961300	-0.14336200	0.41135200
H	-6.13651500	-1.26382900	-1.40365100
H	-5.35161600	0.98946800	2.15136700
H	-6.95268000	-0.17330700	0.66370200

A.4.2.3. $C_6H_4(PSi(SiMe_3)_2Sn$ *cis*

[C6H4P(Si(SiMe3)3)2Sn] cis
Energy: -9973.35519531

C	0.70720600	1.58937100	-0.70007900
C	-0.70720300	1.58938700	-0.70014400
C	-1.37948800	2.81310200	-0.61129800
C	-0.69561700	4.00704700	-0.49768700
C	0.69567800	4.00702900	-0.49762700
C	1.37952400	2.81306300	-0.61117500
H	-2.46134000	2.81906200	-0.62934800
H	-1.24392900	4.93787700	-0.41439800
H	1.24400800	4.93784200	-0.41428700
H	2.46137900	2.81899000	-0.62912800
P	-1.60759700	0.03431900	-0.92739300
Si	-5.20652700	1.01752800	-1.54466200
Si	-3.67814600	0.03646300	-0.01097000
Si	-3.74922800	1.00844800	2.15366600
Si	-4.22688800	-2.27185000	0.17189200
C	-4.66921100	2.71434100	-2.16448800
H	-3.70516800	2.67563400	-2.67510300
H	-5.40989700	3.08241000	-2.88104000
H	-4.59940500	3.44990900	-1.36044400

C	-6.88488700	1.22077500	-0.70459500
H	-6.82890100	1.91816900	0.13446700
H	-7.61275200	1.62190600	-1.41604400
H	-7.27745100	0.27566900	-0.32593500
C	-5.38569800	-0.10121100	-3.04980200
H	-4.41657000	-0.27705000	-3.52199400
H	-5.81613700	-1.07122700	-2.79397600
H	-6.03937600	0.36640700	-3.79188800
C	-5.27799300	0.35155000	3.04712800
H	-5.36003700	0.81915500	4.03285600
H	-6.19404100	0.57737800	2.49700400
H	-5.23617500	-0.72871000	3.19775400
C	-3.88649000	2.88836600	2.12020000
H	-4.75368100	3.22813500	1.54955300
H	-3.99986300	3.26117800	3.14282700
H	-2.99525100	3.35130300	1.69477200
C	-2.20534900	0.52404200	3.11061900
H	-2.10198100	-0.56003800	3.18595800
H	-1.30832900	0.91025000	2.62324500
H	-2.24022800	0.93109100	4.12533900
C	-6.09265600	-2.45135100	0.38826800
H	-6.34178300	-3.50673200	0.53345400
H	-6.46765900	-1.90068100	1.25269400
H	-6.63552600	-2.10482300	-0.49328000
C	-3.72625400	-3.23546200	-1.36732900
H	-4.17581900	-2.82502200	-2.27257300
H	-2.64375100	-3.24369700	-1.51001900
H	-4.05417100	-4.27495200	-1.26950400
C	-3.38514100	-3.05394100	1.66742300
H	-2.29739400	-2.97641300	1.60927800
H	-3.70476800	-2.59477000	2.60484500
H	-3.63666400	-4.11762800	1.71641100
P	1.60755900	0.03427200	-0.92720300
Si	3.67817400	0.03644700	-0.01096500
Si	5.20641800	1.01756900	-1.54475100
Si	4.22692300	-2.27187100	0.17183200
Si	3.74935500	1.00839800	2.15368900
C	4.66898500	2.71436000	-2.16453600
H	3.70490600	2.67561400	-2.67507900
H	4.59920400	3.44992000	-1.36048200
H	5.40960300	3.08246400	-2.88113900
C	5.38553700	-0.10117200	-3.04989500
H	6.03914800	0.36646600	-3.79202800
H	5.81603000	-1.07116800	-2.79408900
H	4.41638500	-0.27705200	-3.52202400
C	6.88482200	1.22087500	-0.70478500
H	7.27744500	0.27578200	-0.32615400
H	7.61262700	1.62203800	-1.41627800
H	6.82885900	1.91826300	0.13428300
C	3.88612800	2.88835500	2.12024900
H	3.99956000	3.26117100	3.14286800
H	4.75314300	3.22836500	1.54947800
H	2.99470400	3.35107200	1.69496900
C	5.27843800	0.35187500	3.04688300
H	6.19433400	0.57793100	2.49660000
H	5.36053800	0.81949700	4.03259700
H	5.23691100	-0.72839500	3.19751400
C	2.20576400	0.52356900	3.11088900
H	1.30855400	0.90955900	2.62369100
H	2.10269100	-0.56054100	3.18621100
H	2.24072100	0.93059000	4.12561800
C	3.38515800	-3.05398800	1.66733700
H	3.70485900	-2.59490100	2.60477500
H	2.29741500	-2.97636100	1.60923700
H	3.63659100	-4.11770000	1.71625300
C	3.72628200	-3.23543600	-1.36741600

H	4.17582400	-2.82495400	-2.27265200
H	4.05421700	-4.27492400	-1.26963700
H	2.64377600	-3.24368200	-1.51008900
C	6.09269000	-2.45139200	0.38820300
H	6.34179900	-3.50677900	0.53337900
H	6.63556900	-2.10486700	-0.49334000
H	6.46769800	-1.90073800	1.25263600
Sn	-0.00004700	-1.80901900	-0.51367900

A.4.2.4. $C_6H_4(PSi(SiMe_3)_2Sn$ *trans*

[C6H4P(Si(SiMe3)3)2Sn] trans
Energy: -9973.35399585

C	0.67816000	-1.58884000	0.19401200
C	-0.67817400	-1.58882800	-0.19381500
C	-1.32910100	-2.81625700	-0.36838400
C	-0.67171000	-4.01539500	-0.18147000
C	0.67170200	-4.01540700	0.18152100
C	1.32908600	-2.81627800	0.36851700
H	-2.36991700	-2.82359700	-0.66589800
H	-1.20034400	-4.95010200	-0.32529800
H	1.20033500	-4.95012200	0.32529300
H	2.36989800	-2.82362500	0.66604600
P	-1.50944300	-0.03036100	-0.61057300
P	1.50946800	-0.03041400	0.61087700
Si	3.69034900	-0.02211300	-0.03007800
Si	4.32179900	2.26738600	0.12892700
Si	4.90550300	-1.31039800	1.57405400
Si	3.84207900	-0.71916800	-2.29209200
Si	-4.90528700	-1.31030000	-1.57432400
Si	-3.69039800	-0.02213600	0.03007700
Si	-4.32189200	2.26735100	-0.12883900
Si	-3.84227100	-0.71932900	2.29206800
C	3.87671300	-1.45721600	3.14392700
H	2.93290200	-1.97896900	2.97463700
H	4.43479700	-2.00533700	3.90892400
H	3.63142800	-0.47181500	3.54559700
C	5.32890600	-3.03366700	0.92959300
H	4.45472100	-3.60851600	0.62094300
H	6.00644400	-2.97720800	0.07440600
H	5.83741400	-3.60088700	1.71501700
C	6.54952700	-0.50668600	2.03251500
H	6.41379000	0.45735100	2.52606300
H	7.08241700	-1.16040100	2.72967300
H	7.19376800	-0.35553300	1.16431200
C	3.69004400	-2.58285000	-2.51579300
H	2.74032800	-2.95829000	-2.13190500
H	3.73691500	-2.82053500	-3.58309000
H	4.49550300	-3.12686100	-2.01996800
C	2.46050800	0.10412200	-3.26782900
H	1.48189500	-0.21067500	-2.89861200
H	2.50406600	1.19261800	-3.20440700
H	2.52833600	-0.17445300	-4.32368700
C	5.51497100	-0.18386300	-2.98601700
H	6.34421100	-0.60837800	-2.41509100
H	5.61810500	-0.52520500	-4.02026800
H	5.62944400	0.90194100	-2.98499300
C	3.77788700	2.96865800	1.79110600
H	4.22956200	2.42519100	2.62383100
H	4.07588500	4.01785900	1.87540300

H	2.69413100	2.92017400	1.91575100
C	3.57274500	3.29820700	-1.26032100
H	3.96450800	2.99792200	-2.23463700
H	2.48428400	3.23204800	-1.29826600
H	3.83468200	4.35005400	-1.11017400
C	6.19237700	2.45773500	-0.02880200
H	6.57382100	2.00912700	-0.94819400
H	6.43733700	3.52385200	-0.05741100
H	6.73208200	2.01617900	0.80825900
C	-3.87628900	-1.45690000	-3.14408200
H	-2.93253100	-1.97873500	-2.97475200
H	-4.43430300	-2.00485900	-3.90924700
H	-3.63090000	-0.47144100	-3.54554000
C	-6.54926100	-0.50657000	-2.03293200
H	-6.41348900	0.45764300	-2.52612500
H	-7.08190000	-1.16010800	-2.73045000
H	-7.19374800	-0.35578000	-1.16484900
C	-5.32870000	-3.03364400	-0.93007400
H	-4.45451900	-3.60843200	-0.62129800
H	-6.00640200	-2.97729700	-0.07501100
H	-5.83700700	-3.60086200	-1.71563000
C	-6.19245900	2.45761900	0.02913000
H	-6.43747900	3.52372400	0.05767300
H	-6.73226000	2.01594700	-0.80780800
H	-6.57375100	2.00908000	0.94861900
C	-3.77820300	2.96863600	-1.79108500
H	-4.22985900	2.42509100	-2.62376800
H	-4.07635200	4.01779400	-1.87538000
H	-2.69444700	2.92030100	-1.91579600
C	-3.57262400	3.29818500	1.26028300
H	-3.96414400	2.99786500	2.23468600
H	-2.48415000	3.23207800	1.29797200
H	-3.83463600	4.35002600	1.11021500
C	-5.51521500	-0.18411000	2.98592900
H	-5.61843800	-0.52559600	4.02012400
H	-5.62968600	0.90169400	2.98504900
H	-6.34440000	-0.60854900	2.41486900
C	-3.69024200	-2.58302300	2.51570100
H	-4.49557600	-3.12702100	2.01965700
H	-2.74043000	-2.95842300	2.13201400
H	-3.73735500	-2.82077400	3.58297300
C	-2.46076700	0.10394700	3.26790900
H	-1.48213800	-0.21089600	2.89877200
H	-2.50427600	1.19244500	3.20445500
H	-2.52869100	-0.17459900	4.32376800
Sn	0.00004200	1.83547800	0.00007300